

CHAPTER-I

INTRODUCTION

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Overview

Basic need of modern civilization is energy and its production from fossil fuels causes hazardous effect on the environment. This motivates to use the clean energy sources. Solar energy has best potential to fulfill the energy demand in future. Sunlight is not only the most plentiful energy resource on earth, but it is also one of the most versatile, abundantly available and free of cost throughout on the planet, converting readily to electricity, fuel and heat without emitting pollutant elements. The time line of solar energy research shows the development of photovoltaic technology. The way of conversion of sun energy into electrical energy divides the photovoltaic technology into different generations. The literature survey describes different solar cell structure. Last part of this chapter presents the scope of development of the solar cells using low cost techniques and way of research performed.

1.1. Introduction and motivation

The energy plays the most crucial role in the modern human civilization. Mankind uses the fossil fuels as energy source from millions of years. Presently, most of the energy demand (upto 90%) is fulfilled from the fossil fuels in the form of coal, natural gases, petroleum product etc. The burning of these fuels emits the gases like CO₂, CH₄, NO_x, sulphur etc. and remains their residuals in an environment. These gases are also known as green house gases. The green house gases traps the infra-red radiation within the earth's atmosphere, thereby increasing the "global" atmospheric temperature (approximately 4°C of earth temperature will increase in this century) [1-3]. During the past few decades, all nations have become extremely concerned with the effect of global warming. The emission of these gases depends on the use of the fossil fuels and cut down the dependency on fossil fuels is one solution to reduce effect of global warming. Dependency on renewable energy sources in power sector is a need of the universe, since fossil fuel resources are rapidly depleting and responsible to emission of green house gases. The transformation of energy policies is not individual government effort but world-wide political issue. The several nations have been transfer their energy policies; towards utilization of clean energy sources instead of use of fossil fuels.

Clean energy sources will play vital role in the future which includes: wind, geothermal, biomass, tidal and hydroelectric etc. out of these none of the technology

is scalable to fulfill future energy demands. Only solar energy is having potential to fulfill the energy demand in future. For a scale, consider; sun provides 130 TW energy daily. Current global energy consumption occurs at the rate of 13.5 TW, projected to rise to 40.8 TW in 2050. Today, in just one hour, the sun provides enough power to supply our energy needs for an entire year which is available free of cost. In the universe and particularly country like India, an average intensity of solar received is 200 MW/km (megawatt per square kilometer) with 250-325 sunny days in year [4]. Hence, solar energy is having capacity to fulfill the energy demand of urban civilization without harming the environment.

1.2. History of photovoltaic systems

In 1839, Edmund Becquerel a French physicist has discovered photoelectric effect. This discovery motivates to the scientist all over the world to make an efficient energy device that will convert maximum sun energy into electricity. The photovoltaic device having potential to convert sunlight into electrical potential by a sequence of events: the absorption of light, generation of charge carriers (electrons and holes) and the transport of charge carriers to electrodes. The world's breakthrough discoveries in the photovoltaic system are included in the table 1.1. The generation of electrical energy from solar power can be divides photovoltaic (PV) devices technology into three different classes, which is explained in section 1.3.

Table 1.1: Timeline of the major breakthroughs in development of PV cells [5,6]

Year	Discovery
1839	First report on photoelectric effect by Edmund Becquerel
1876	Solid state device based on Selenium by William Adams and Richard Day
1916	Experimental proof of the photoelectric effect by Millikan
1923	Albert Einstein received the Nobel Prize for his theories; explaining the photoelectric effect
1951	A grown p-n junction enabled the production of a single-crystal cell of Germanium
1954	First report of Silicon solar cell ($\eta \sim 6\%$) by Chaplin, Fuller and Pearson
1958	USA was launched "Vanguard I" satellite in space working on photovoltaic cells.
1960	Hoffman Electronics achieved 14% efficient PV cells.
1970's	The energy crisis, force to search alternative energy source. Thereafter solar cell research rapidly develops as alternative energy source.
1990's	First scalable reports based on low cost nanostructured solar cell working on PEC principal reported by M. Gratzel.

1.3. Types of solar cells

The photovoltaic (PV) cells generate electric power under illumination of natural or simulated sunlight. The human being develops such devices for the generation of energy; these devices can be categorized into different types on the basis of stepwise development [7].

1.3.1. First generation solar cells

The basic building block of first generation (1G) solar cells technology is Silicon; either single crystalline Silicon (s-Si) or multi-crystalline Silicon (mc-Si). The conventional PV cell modules are built by 200-250 micron thick crystalline Silicon wafer and majority of the cost utilized to extract crystalline Silicon from sand, then to purify and finally the doping of phosphorous and boron to make p-type and n-type Silicon. The 1G PV cells are operated on the simple p-n junction diode principle where electron-hole charge generated under illumination of a light and its separation occurs in a p-n junction: i.e. at the interface of p-type and n-type semiconductor generates a built-in potential. At the junction itself, a depletion region free of mobile carriers is formed, in which the electric field is present. The commercial production of 1G solar cell modules started since 1963 and now about 90% of global PV cells market is concerned by 1G solar cell. The efficiency of 1G ranges from 14% to 19%.

1.3.2. Second generation solar cells

Second generation (2G) of PV cells market is based on; to remove the unnecessary material production cost to obtain pure Silicon and search alternative to crystalline Silicon. 2G PV cells are fabricated by single junction devices; keeping in mind that to reduce the processing cost of material; while maintaining the efficiencies of 1G PV. 2G solar cells are fabricated by amorphous-Silicon (a-Si), CuInSe (CIS), CuIn(Ga)Se₂ (CIGS), CdTe/CdS and polycrystalline Silicon (p-Si) deposited on low-cost substrates such as glass, polymers and metals. 2G PV cells technologies is based on efficient light trapping properties of CdTe, CIS, CIGS and a-Si than c-Si or mc-Si, also the thickness of absorbing materials ranges in 1-10 micron, hence responsible to reduce the production cost of the PV devices. Meanwhile 2G technology has been received much attention in the last few years, due to their imperative parameters such as, it requires less semiconducting material to fabricate the PV modules, can be synthesized on flexible substrate and light weight structures. The 2G technology can be categorized into three types as follows.

A) Amorphous Silicon PV cells

The PV cells constructed with a-Si shows efficiency range from 4% to 8%. The PV cells of a-Si are advantages because it can be deposited on comparatively low cost large area substrates or even flexible substrate, but the major drawback is reduction in power output with time.

B) Cadmium telluride PV cells

These types of solar cells are cheapest in thin film PV technology and having efficiency 16%. But toxicity of cadmium and availability of tellurium are the major problems with these types of solar cells; hence limits its use.

C) CIS and CIGS PV cells

These types of solar cells are most successful in PV industries and have been commercialized by many companies. (e.g. Würth Solar, Solibro, Miasole, Nanosolar, Shellsolar, Avancis, Solar Frontier and Honda Soltec). Currently, CIS and CIGS PV cells efficiency ranges from 7% to 16%.

1.3.3 Third generation solar cells

Now a day's, third generation (3G) solar cell technology is an emerging technology and still in research phase. The 3G PV solar cell includes nanostructured solar cells (i.e. organic photovoltaic (OPV), dye-sensitized cell (DSSC), ETA solar cell, quantum dot sensitize solar cell (QDSSC) and organic-inorganic hybrid solar cell etc.) While, these cells working on same p-n junction solar cell phenomenon but having separately photoengraved and charge carriers that will helps to faster recombination in devices and this will ultimately increase the efficiencies of the cell. These types of PV cells are far behind, when compared with the efficiency point of view to the conventional PV cell have number of advantages over 1G and 2G PV cells. It is consider that 3G solar cells are potential to overcome the Shockely-Queisser limit of 31-41% power efficiency of the single band gap material solar cell devices.

A) Dye sensitized solar cells (DSSC)

In 1991, Professor Michael Gratzel at EPFL in Switzerland first demonstrated the DSSC efficiently by using TiO₂ and ruthenium metal dyes and with 11% efficiency. This is the mildstone in 3G PV research. DSSC were synthesized between two glass substrates in sandwich type structure, but thereafter it was also reported on flexible substrates. The DSSC works on photoelectrochemical (PEC) principle. In DSSC high surface area TiO₂ plays dual role 1) act as window layer for visible light;

which further absorbed by dye molecules and 2) receives photo generated electron from the dye molecules and holes are passed to the other side of the dye. Then the circuit is completed by redox couple in electrolyte, which can be liquid or solid. The last 20 years research and development effort lead to develop commercial devices by Dyesol, EPFL, G24i, Mitsubishi and Peccell. DSSC has many advantages over conventional PV cells as it is colorful, low processing cost and can be synthesized on flexible substrates. However, the major disadvantage is that dyes in these cells can be degrade under heat and UV light, furthermore solvent evaporation is difficult to avoid due to improper sealing.

B) Organic photovoltaic (OPV) solar cells

This is one of the alternative technology immerging in recent years than the conventional PV cells. The solar cells are constructed by using organic or polymer materials. Organic cells are constructed on variety of substrates irrespective of their shape and size and by low cost synthesis technique (i.e. printing and coating). OPV cells are lightweight; flexible which makes them ideal for mobile applications. Furthermore, it will be fitted on a variety of uneven surfaces. This makes them useful for portable applications. The leading developers in OPV technology industries such as Konarka and Plextronics are developed and make it commercially available in the market.

C) Nanostructured solar cells

Now days, nanostructured PV cells are immerging as an alternative to conventional Silicon solar cell technology. These types of device structures are under research and development and which are rely on use of composite/heterostructure materials such as quantum dots/wires, quantum wells, ETA solar cells, inorganic organic hybrid structures etc. These solar cells are working on the similar principle that of DSSC. Nanostructured wide band gap metal oxide (MO) plays dual role in device structure; first to provide high surface area for the growth of a light absorber materials in layer structure, also absorbs UV part of incident light which may harm the absorber layer and second, receives the photo-generated electron from the absorber materials and finally execution of circuit completion by redox couple either organic or inorganic materials like liquid or solid. These are most advantageous PV cell technology in future, because; 1) to overcome the Shockely-Queisser limit of 31-41% power efficiency of conventional technology, 2) the inorganic light absorber materials are more stable, cheaper, colorful and tune their prperties according to their

size and shape, 3) the devices can be synthesized by low cost wet chemical deposition techniques which may reduce the processing cost. The reported efficiency of different generations of solar cells is listed in the table 1.2.

Table 1.2: Efficiencies of lab scale devices [8]

Type of solar cell	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	η (%)	Generation of solar cell
Mono crystalline Silicon	0.70	42	84	24.7	1G
Poly crystalline Silicon	0.66	38	81	20.4	1G
Amorphous Silicon	0.89	16.8	67	10.1	2G
CdTe	0.85	26.1	76	16.7	2G
CuInGaSe ₂ (CIGS)	0.72	33.7	80	19.5	2G
Multi-junction (GaInP/GaAs/Ge)	2.62	14.4	85	32	3G
DSSC	0.73	22	65	10.4	3G
Organic	0.88	9.4	63	5.2	3G
ETA	0.44	15.7	60	4.2	3G
Organic tandum	1.59	6.2	62	6.1	3G

1.4. Aim and scope of ETA solar cell devices

In last few decades, the research in PV technologies have been concentrated onto search a new efficient device; that can be convert maximum sunlight into electricity. The outcome of these efforts is focusing us to transformed interest towards utilization of nanocrystalline materials for solar cell application; due to their unique structural, optical and electrical properties depending on their size and shape. Application of these features in photovoltaic device has led to develop novel solar cell structure. DSSC is one of the devices investigated much in last few decades and consider as an alternative to conventional solar cell. These devices are working on PEC principle, but have their own limitations; those forces to search new photovoltaic materials and devices. The nanostructured solar cell is working on the similar principle of DSSC. This overcomes the problems of DSSC and replace unstable dye layer by stable inorganic metal chalcogenides nanoparticles layer in the device structure.

As a consequence of the problems faced by the DSSC, the ETA solar cell structure has potential to overcome it. The ETA solar cell structure was developed in the late 1990's and use the concepts from both DSSC and thin film solar cells. The foundation of nanostructured solar cells concept is the establishment of a layer heterostructure between large internal surface area of wide band gap MO and

extremely thin film absorber layer consisting of nanoparticles of a narrow band gap metal chalcogenides in the solar cell to improve light harvesting and stability as compared to DSSC.

The cell borrows the principle of separating charge generation and transport from DSSC. ETA consisting of nanoparticles cell; light is absorbed by an extremely thin film and generates electron hole pair. (The generation of electron hole pair in semiconductors is explained in section 2.1 of chapter-II). The built-in electric field across this layer separates the charge carriers. The electrons and holes are then transported through the liquid electrolyte and n-type wide band gap semiconductors, respectively.

Figure 1.1. shows a basic ETA solar cell structure consisting of inorganic narrow band gap semiconducting materials. In most of the cells, a transparent conducting oxide (TCO) glass is used as a substrate which allow light to pass. This light is utilized by layer heterostructure and act as front contact to the cell. On to the TCO, layer heterostructure is synthesized sequentially by depositing thin films of wide band gap metal oxide (MO) followed by narrow band gap metal chalcogenides as a sensitizer. The circuit complied by using synthesized nanostructure as an anode, polysulphide electrolyte (S²⁻/S_n²⁻) as a redox couple and platinum as a back contact. MO fabricated by using nano-sized particles to form porous layer with interconnected nanoparticles leading to high surface area.

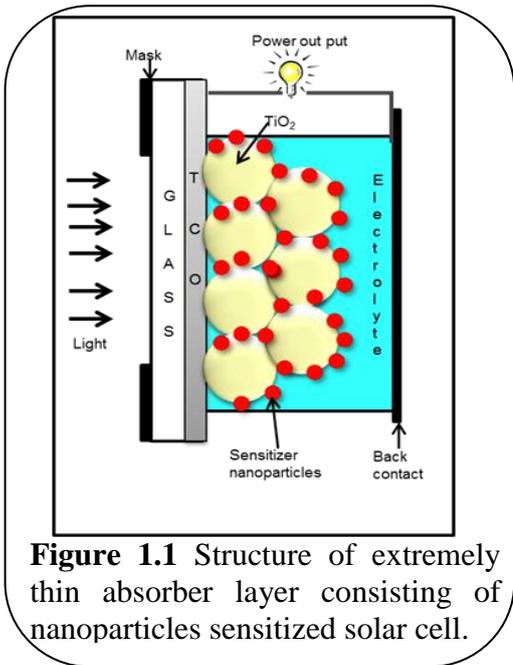


Figure 1.1 Structure of extremely thin absorber layer consisting of nanoparticles sensitized solar cell.

However, the wide band gap MO layer is not intended to generate charge carriers within the cell. Therefore, the amount of the light absorbed by this layer should be small. Consequently, MO must be act as window layer for visible light with typically band gap > 3 eV and the conduction band edge position is lower than that of the absorber materials. Hence, the MO such as TiO₂, ZnO, SnO₂ have been commonly used as a widow layer within the ETA solar cell. In proposed research, we have used TiO₂ as a widow layer synthesized by sol-gel derived low cost spin coating technique.

The generation of charge carrier (electron-hole pair) occurs within the absorber layer deposited on wide band gap MO layer. Hence, the band gap absorber ETA layer should be in the range of 1.4 eV to 2.4 eV to utilize the maximum portion of the visible light from the solar spectrum. In an ideal device, this coating covers the entire internal surface of the nanostructured MO layer. As a result, the thickness of the absorber can be reduced to less than a few hundred nm which reduces the probability of charge carrier recombination within this layer and absorbs more light.

The proposed research focuses the narrow band gap metal chalcogenides such as CdS, CdSe, Bi₂S₃ and Sb₂S₃ which can acts as an absorber layers. The proposed research is focused onto use of linker/ligand free simple and low cost wet chemical synthesis route at room temperature for the synthesis of ETA layer consisting of nanoparticles on porous TiO₂ surface for solar cell application. The constructed device has the structure

FTO/TiO₂/thin absorber layer/hole conductor (liquid electrolyte)/Platinum (back contact).

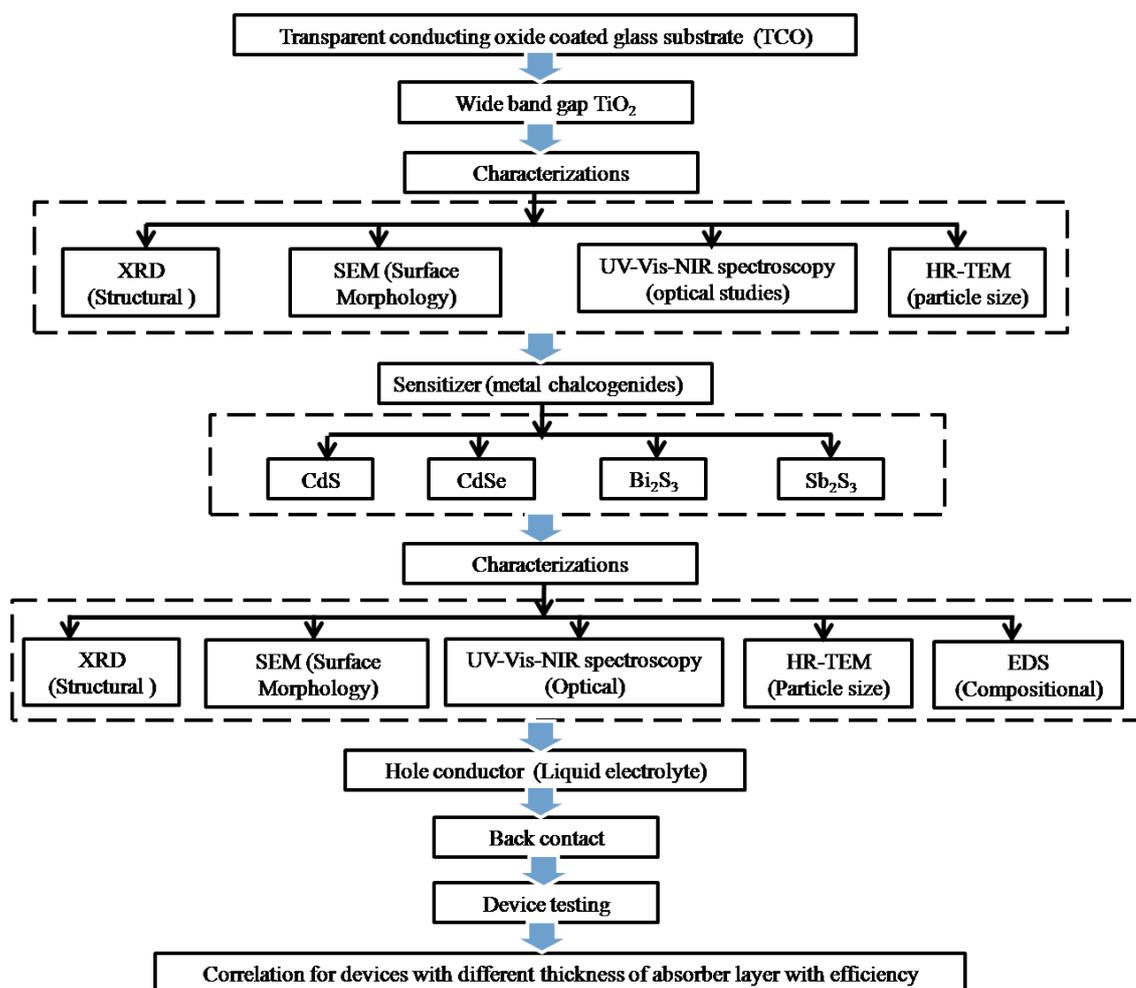


Chart 1.1 Flowchart summarizes the stepwise development of laboratory grade device

The flowchart 1.1 summarizes the step wise synthesis, characterizations and construction of the extremely thin film consisting of nanoparticles as absorber layer in solar cell device.

In this work, three major aspects have been focused (i) synthesis of TiO₂ thin films, (ii) Use of soft chemical technique to synthesize different thickness of thin absorber (sensitizer) layer on TiO₂ electrode and (iii) construction of sandwich type devices using polysulphide as a liquid electrolyte and platinum as a back contact.

1.5. Literature survey

This survey is done towards the general understanding of the construction of ETA solar cells by using nanostructured semiconducting materials. Initially, attempt has been focused for the recent accomplishment in synthesis and application of wide band gap MO (TiO₂) in the device grade solar cell applications. Then, study is made for the utilization of various narrow band gap metal chalcogenides (such as CdS, CdSe, Bi₂S₃, Sb₂S₃) either in the form of extremely thin film absorber layer or nanoparticles in thin film form for ETA solar cell application.

1.5.1. Titanium dioxide

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium with chemical formula TiO₂. Recently, scientific and research community have shown their great interest to synthesize titanium dioxide (TiO₂) for device grade applications because of its excellent properties such as easily available, non toxic, safe, environmental friendly and cheap. These advantages make TiO₂ beneficiary towards number of device grade applications such as, energy harvesting, hydrogen production [9,10], photonics [11,12], sensors [13], cancer treatment [14] and water purification [15]. TiO₂ has been available in three different structure types: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic). All of these crystalline forms of TiO₂ occur in nature as mineral, but only rutile and anatase have been able to be synthesized in pure form. The review in this filed suggest that most stable phase of TiO₂ are anatase and rutile, extensively studied by research community in entire world. The physical and optical properties of TiO₂ are listed in table 1.3.

Synthesis and applications of TiO₂ toward solar cell application

Titanium dioxide has important material since ancient time, where it can be used as white pigment. In early 20th century, the commercial productions of TiO₂ has

been widely used in sunscreen, paints, toothpaste many other. There was a report on the photo bleaching of dyes by TiO₂ both in vacuum and in oxygen in 1938 [17]. Recently, various forms of TiO₂ have been synthesized in the form of powders, thin film and nanocrystals as a nanoparticles [18-19], nanotubes [20-22], nanofiber [23, 24], nanobelts [25, 26] and nanorods [27, 28] etc. by number of synthesis techniques.

Table 1.3: The structural properties of different TiO₂ morphology [16]

Compound	Rutile	Anatase	Brookite
Formula	TiO ₂	TiO ₂	TiO ₂
Molecular weight (g/mol)	79.89	79.89	79.89
Molecules per unit cell (Z)	2	4	8
Crystal structure	Tetragonal	Tetragonal	Orthorhombic
Most stable surface	(110)	(101)	---
Unit cell parameters			
a (Å)	4.58	3.78	9.184
b (Å)	4.58	3.78	5.447
c (Å)	2.95	9.78	5.145
Unit cell volume	62.07	136.25	257.38
Electron effective mass	9-13 m _e	~1 m _e	--
Mobility of electron in thin film form	0.1 cm ² /Vs	0.1-0.4 cm ² /Vs	--
Molar volume	18.693	20.156	19.377
Density (g/cm ³)	4.2743	3.895	4.123
Band gap (eV)	3.02	3.2	3.1
Refractive index			
⊥ to c axis	2.60	2.55	2.57
∥ to c axis	2.89	2.48	2.69
Dielectric constant			78
⊥ to c axis	89	31	
∥ to c axis	173	48	
Cationic radius (Ti ⁴⁺) (Å)	0.605	0.605	0.605
Anionic radius (O ²⁻) (Å)	1.36	1.36	1.36

In 1972, Fujishima and Honda discovered the photocatalytic splitting of water on TiO₂ electrodes illuminated with UV light under no external bias [29]. This event is marked as major breakthrough for the use of TiO₂ in the device grade applications in PEC cells. Thereafter, researchers of many streams including physicist, chemist, biologist, engineers have investigated different forms of TiO₂ thin film or powder in number of devices grade applications.

Among new materials being developed for solar cells, photo-catalytic and other applications, TiO₂ remains one of the most promising materials, due to its low cost, chemical inertness, eco-friendly nature and photo stability. Several excellent

properties of TiO₂ are available such as chemical inertness, superior light scattering characteristics, thermodynamic stability, better charge transport, lower conduction band edge position, large band gap, easily process in laboratory etc. These properties make it suitable for the PEC cell application. Gratzel et al have reported DSSC with nanoporous TiO₂ film used as photoanode that provides high surface area for the adsorption of dye molecules, act as window layer and receives charge carrier from excited dye molecules and achieved 7% efficiency [30] and increased efficiency further 4% [31]. Many groups have reported various TiO₂ nanostructures morphology with various dye molecules for the DSSC application [32-35]. Although the DSSC concept is comparatively simple, a lot of disputes still remain. Because, charge generation and injection from the dye is most efficient when the dye is coated in a monolayer upon the surface of the nanostructured TiO₂.

However, the deposition of the dye molecules proceeds via self-assembled chemisorptions and gets aggregated. This can obstruct to transfer electron from the dye to the TiO₂ as well leading to charge carrier recombination as a result of intermolecular quenching. [36] In addition, the excited dye molecules can be quenched by the oxidised redox species in the electrolyte, thereby reducing the performance of the cell [37]. Another drawback of using dyes is that the photocatalytic properties of the TiO₂ under UV light make the organic dyes more susceptible to degradation than inorganic materials [38].

The stability of dye molecules is major issue in DSSC which enforce us to search new types of absorber/sensitizer. Hence, nanostructured solar cell is an emerging as an alternative to conventional solar cell technology, which works on similar principle of DSSC. Where, the device constructed with inorganic narrow band gap semiconducting material either in the form of thin absorber layer or quantum dot layer as a light harvester instead of dye [39]. The conventional inorganic semiconductors can absorb over broad wavelength range (i.e. the material will absorb photons $\geq E_g$ of the semiconductor), whereas dye molecules are known to display a Gaussian (bell shaped) type absorption profile, hence reducing the absorption of light in the DSSC. The pioneering work in nanostructured solar cells was initiated by Konenkamp et al where the anatase porous TiO₂ film act as photoanode and provides high surface area for the adsorption of absorber layer, also; electron can be recombined much faster [40]. Ernst et al have synthesized nanostructured TiO₂ film by spray pyrolysis technique and further forms heterostructure with II-VI compound

for ETA solar cell application [41]. In 2001, Earnst et al. explains the concept of ETA solar cell with CdTe as a absorber layer of on porous TiO₂ and achieved 1.17% efficiency [42]. Tennakone et al has constructed photovoltaic cell by using TiO₂ nanoporous and achieved 0.13% efficiency [43]. Recently, Itzhaik et al reported 3.37% efficiency of ETA solar cell by introducing In₂S₃ buffer layer between porous TiO₂ and absorber layer of Sb₂S₃ [44].

1.5.2. Cadmium sulphide (CdS) as light harvester

Since the development of nanotechnology, semiconductor materials have attracted extensive interest because of their fundamental importance and wide range of potential applications in nanoscale devices. Among them, cadmium sulphide is an important binary metal chalcogenide of group II-VI having chemical formula CdS. It has been used in variety of applications due to its excellent physical and chemical properties changed consequently by tuning of the size. The bulk CdS is having 2.4 eV direct band gap and yellow color. The CdS shows excellent optical properties and absorbs wide range of visible light, also varies the absorption range in visible region of light, accordingly their shape and size. Due to quantum confinement effect, the CdS changes their color from greenish to slightly orange. The CdS can be easily synthesized by various physical and chemical techniques like sol-gel [45], electrodeposition [46], gas evaporation [47, 48], spray pyrolysis [49], micelles [50], CBD [51], SILAR [52] and doctor-blade [53]. Also CdS can easily forms heterostructures with other semiconducting materials. These advantages make CdS make it beneficiary toward solar cell application.

Literature review showed that, CdS thin film shows photovoltaic activity under illumination of light. In 1994, Torimoto et al prepared various size CdS microcrystal in thin film form with viologen functionalized thiol using inverse micelles technique and studied the effect of ligand molecules on PEC behavior of CdS [50]. Seminal group have also studied PEC behavior of size quantized CdS thin film on gold substrate, for the study they sequentially deposited S and Cd layer on Au substrate by applying potential [54]. Lade et al have studied the PEC properties of electrodeposited CdS thin film from aqueous and non-aqueous bath onto different substrates by using polysulphide as a electrolyte and graphite as a counter electrode in dark and illumination of light [46]. In 2006, Jia et al achieved 2.2% efficiency under illumination of 35 mW/cm² simulated light, where CdS nanocrystalline thin film

synthesized by doctor-blade technique on indium doped tin oxide substrate (ITO) [53]. Hilal et al have studied the effect of cooling on PEC properties of chemically deposited thin film of CdS on FTO substrate [51]. Recently, Pawar et al reported PEC behavior of CdS thin film deposited on FTO substrate by aqueous alkaline chemical bath [55]. This shows that CdS is photoactive material, which has an ability to convert solar energy in the form of photons to electricity. Ahire et al have reported PEC behavior of different stoichiometric compositions of CdS and Bi₂S₃ thin film on ITO substrate, synthesized by low cost SILAR technique [56]. In the CdS/CdTe solar cell structure, CdS act as a window layer material. On the other hand; in layer heterostructure between MO and CdS, either in the form of extremely thin absorber layer or quantum dots layer and works as a light harvester. The different sized CdS nanoparticles in ETA or QD's layer can be synthesized either by sophisticated techniques or linker assisted technique. An overview of CdS as absorber layer in ETA as well as QD sensitizer solar cell with detailed structured and efficiencies are listed in table 1.4.

1.5.3. Cadmium selenide (CdSe) as light harvester

Cadmium selenide belongs to II-VI binary semiconductor composed of the Cd²⁺ and Se²⁻ ions having chemical formula CdSe. Different size and shaped CdSe nanoparticles can be synthesized by various synthesis techniques either in-situ chemical technique [57-59] or ex-situ chemical techniques [60-61]. The CdSe has measured ~1.7 eV direct band gap [62], hence it has an ability to absorb wide range of visible light ($1.1 \text{ eV} < E_g < 1.8 \text{ eV}$, with optimal $E_g \sim 1.5 \text{ eV}$). CdSe thin films have been extensively studied as a potential candidate as a light harvester material in solar cells [62-66]. CdSe easily forms layer heterostructure with other semiconducting materials; hence it is a promising candidate's in heterostructure devices. Tong Ju et al have fabricated solar cell device of complete inorganic materials with different thicknesses of CdSe and CdTe and achieved maximum 3.02% efficiency with 100 nm CdSe and 300 nm CdTe in heterostructure device [67]. CdSe also used in hybrid solar cells, Brandenburg et al have studied the influence of different CdSe particle size in CdSe/P3HT hybrid solar cell device [68]. In nanostructured solar cells, CdSe having an ideal band edge position to transfer excited electron to low lying conduction band edge of wide band gap MO's surface. In this concern large numbers of reports are available, either in ETA or QD's sensitized solar cells. In order to synthesize nanostructured solar cells, CdSe act as an active light harvester. In 1993, Du Lie and P

V Kamat reported the pioneering work based on photovoltaic behavior of heterostructure between TiO₂ and CdSe [69]. Thereafter, Fang et al reported CdSe/TiO₂ heterostructure with introducing silicotungstic acid (STA) during deposition of CdSe layer on pre-deposited TiO₂ thin film; this structure improves the photovoltaic performance of the device. They compare the effect of STA on devices by observing open circuit voltage (V_{oc}) and short circuit current (I_{sc}) with STA $V_{oc} = 0.55$ V, $I_{sc} = 17$ mA and without STA $V_{oc} = 0.53$ V, $I_{sc} = 12.4$ mA. In 2006, Sankapal et al have synthesized layer heterostructure between electrodeposited nanoporous ZnO electrode and chemically deposited CdSe nanoparticles film and studied PEC performance of the devices under illumination of 100 mW/cm² of simulated light using of polysulphide and polyiodide as an electrolyte. While, device gives the short circuit current density (J_{sc}) of 2.89 mA/cm² and V_{oc} of 0.3 V for polysulphide electrolyte and J_{sc} of 0.43 mA/cm², V_{oc} of 0.62 V for polyiodide electrolyte [70]. Levy-Clement et al have achieved 2.3% efficiency using CdSe thin absorber layer on ZnO nanostructured film [71]. Same group have reported ETA solar cell structures in ZnO/CdSe/CuSCN structure in 2006 [72]. Recently, Feiyan Zhano et al achieved 2.13% efficiency of TiO₂/CdSe cell structure, where TiO₂ nanostructured window layer is modified by using TiCl₄ treatment [73]. An overview of CdSe as an absorber layer is in ETA as well as QD sensitizer solar cell with detailed structured and efficiencies are reported in table 1.4.

1.5.4. Bismuth trisulphide (Bi₂S₃) as light harvester

In last couple of decades, interest in the use of PEC solar cells for low cost of energy conversion has lead to large amount of research to search thin polycrystalline materials with acceptable performances. The thin film of bismuth trisulphide (Bi₂S₃) can be synthesized by various techniques. For PEC cells, prime requirement is that band gap of semiconducting material close to visible light spectrum. The Bi₂S₃ is V-VI compound having 1.7 eV band gap, which is close to visible spectrum, non toxic and easily synthesized by low cost chemical technique [74]. In addition, thin film of Bi₂S₃ having nanocrystalline nature which helps to absorb more incoming incident visible light and convert into electron hole pair in the cell. Mane et al have studied the PEC properties of chemically deposited nanocrystalline thin film of Bi₂S₃ from aqueous and non aqueous medium [74]. The PEC cell performances were carried out by using polysulphide liquid as an electrolyte and carbon as a counter electrode [74-77]. While, Ahire et al have studied the PEC behavior of chemically deposited

(CdS)_x(Bi₂S₃)_{1-x} composite thin film on FTO substrate [56]. Bi₂S₃ easily forms heterostructures with wide band MO's for solar cell device. In this concern, Suarez et al. has synthesized colloidal Bi₂S₃ nanoparticles by hot wire injection technique and further adsorbed on SnO₂ by chemical precipitation technique and studied photovoltaic behavior of PEC cell with polysulphide electrolyte as a redox couple [78]. In 2003, Peter et al. have capped Bi₂S₃ nanoparticles with 3-mercaptopropionic acid and then self-assembled by arrested precipitation technique on the nanocrystalline TiO₂ electrodes via carboxylic linker and reported the tuning of the band gap by varying the particle size, the photovoltaic properties of heterostructure was tested by using 1M Na₂S an Na₂SO₃ as electrolyte under illumination AM1.5 G, simulated sunlight [79]. Even though, Bi₂S₃ has many advantageous among narrowband gap materials; but very less attempts are made for the utilizations towards solar cell application.

1.5.5. Antimony trisulphide (Sb₂S₃) as light harvester

Sb₂S₃ is the promising candidate of group V-VI compound having applications in many optoelectronic devices. A number of techniques have been employed for the preparation of Sb₂S₃ thin films [80-85]. Sb₂S₃ having 1.8 eV direct energy band gap ideal for the conversion of incident visible spectrum of light into electricity. Sb₂S₃ easily forms layer heterostructures with other semiconducting materials, even though; very few attempts have been made towards utilization towards solar cell application. First attempt was made by Savodago et al in 1993; they have chemically synthesized Sb₂S₃ layer using STA on Si. The formed heterojunction was tested under AM 1 illumination and achieved ~5.19% efficiency [86]. Yafit Itzhaik et al reported ETA solar cell having 3.37% efficiency under illumination of 60 mW/cm² simulated light on TiO₂/Sb₂S₃/CuSCN cell structured [44]. In 2010, Shinji Nezu et al reported the light soaking effect of nanocrystalline TiO₂/Sb₂S₃/CuSCN ETA solar cell structure, where they achieved efficiency ~3.7% upto 300 days [87]. Chang et al have reported the highest 5.13% efficiency of solid state nanostructure cells of inorganic-organic heterostructure of Sb₂S₃ and P3HT on the surface of mesoporous TiO₂ electrode, where Sb₂S₃ act as an absorbing material and P3HT as a hole conductor [88]. Sb₂S₃ has similar properties that of CdSe, even though it is very less investigated material in solar cell application due to stability issue.

In entire literature review, most of the inorganic narrow band gap metal chalcogenides are playing crucial role for the generation of electricity from a visible

light in PEC cells. The absorber materials are extremely thin film consisting of nanoparticles forms heterostructures with wide band gap MO's in PEC cell. In most of the reports, colloidal nanoparticles of the narrow band gap materials synthesized by chemical technique such as reverse micelles [50,94,96], linker assisted chemical route [60,61,78,79,89-91,95,99,106-110] and electrochemical [46,54,100,102] route. Reverse micelles and linker assisted routes are ex-situ deposition techniques used for the synthesis of different size QD's of narrow band gap materials. The growth of colloidal nanoparticles is based on the decomposition of metal precursor in liquid medium and successively controlled the recombination. Further, growth was controlled by ligands (organic, aqueous, polymeric or molten glassy matrix) and bifunctional linker molecules used to attach with MO's. However, this route is low cost alternative for the preparation of size tune nanoparticles but it has disadvantages that the bifunctional linker molecules are having molecular chain and that molecular chain affects the charge transportation in the device. Due to molecular chain photo-generated charged carriers transportation path increases, it may also resist to flow of electron and hence restrict the efficiency of the cell [111-118]. However; it is very difficult to control the particle size without using linker/ligand molecules due to possibility of the aggregation of particles.

In this inspiration, we have focused our research to develop linker free novel chemical route to deposit narrow band gap metal chalcogenides on nanostructured TiO₂ and discussed its performance in this thesis.

Table 1.4: Year wise development for nanostructured solar cells.

Year	Window layer	Absorb er layers	Hole conductors	Type of sensitizers layer	J _{sc} (mA/cm ²)	V _{oc} (V)	η (%)	Refer ences
2002	TiO ₂	CdS	Liquid Na ₂ SO ₃	QD	--	--	--	[89]
2003	TiO ₂	CdS	---	QD	--	--	--	[90]
2003	TiO ₂	CdS	-	Nanoparticles			-	[91]
2006	TiO ₂	CdS	CuSCN	ETA	2.3	0.86	1.3	[92]
2007	TiO ₂	CdS	Li- iodied	ETA	--	---	---	[93]
2007	TiO ₂	CdS	Polysulphide	QD	3.44	0.63	1.35	[94]
2008	TiO ₂	CdS	Polyiodide	QD	--	--	--	[95]
2008	TiO ₂	CdS	Polysulphide	QD	1.33	0.26	0.1	[96]
2009	TiO ₂	CdS	Polysulphide	Nanorod	4.85	0.74	1.51	[97]
2009	ZnO	CdS	Polyiodide	QD	2.6	0.44	0.34	[98]
2009	TiO ₂	CdS	--	QD	--	--	--	[99]
2009	TiO ₂	CdS	Polyiodide	QD	2.61	0.76	1.24	[100]
2010	ZnO	CdS	Polyiodide	QD	2.54	0.54	0.4	[101]
2011	TiO ₂	CdS	Polysulphide	QD	7.53	0.49	0.27	[102]
2011	TiO ₂	CdS	Polysulphide	QD	7.20	0.46	1.18	[103]
1998	TiO ₂	CdSe	--	QD	10	0.23	-	[104]

2001	TiO ₂	CdSe	Polysulphide		5.6	0.48	1.2	[105]
2007	ZnO	CdSe	Polyiodide	Nanoparticles	1-2	0.40	~0.3	[106]
2007	TiO ₂	CdSe	Polysulphide	QD	0.2	0.44	0.06	[107]
2008	TiO ₂	CdSe	Polysulphide	Nanoparticles	10.61	0.38	1.4	[96]
2009	TiO ₂	CdSe	Polysulphide	QD	--	---	3.21	[108]
2009	TiO ₂	CdSe	Polysulphide	QD	--	---	0.97	[109]
2009	TiO ₂	CdSe	Polyiodide	QD	--	---	0.78	[109]
2010	TiO ₂	CdSe	Polyiodide	QD	6.95	0.81	3.65	[110]
2011	TiO ₂	CdSe	Polysulphide	QD	10.93	0.49	2.69	[102]
1998	SnO ₂	Bi ₂ S ₃	Polysulphide	QD	--	--	--	[78]
2003	TiO ₂	Bi ₂ S ₃	Polysulphide	QD	--	--	--	[79]
2010	TiO ₂	Sb ₂ S ₃	CuSCN	QD	11.6	0.56	3.7	[87]

1.6. Scope of thesis

It is to coat extremely thin film consisting of nanoparticles onto wide band gap TiO₂ towards solar cells application as a low cost alternative to conventional solar cell technology. In current photovoltaic technology, the cost per watt is mainly high, because most of the efforts and cost required to obtaining pure Silicon. Hence, commercially available cells are not affordable for large scale energy production compared with the available resources. The cost per watt can be lowered by two ways, either lowering the manufacturing cost or increasing the amount of power output for the same cost. The current photovoltaic devices have reached to their maximum theoretical and practical efficiencies and may not be possible to further increase in the efficiencies and reduce the processing cost. Till today, different types of solar cells are available based on Si, GaAs, CdS/CdTe, chalcopyrite, organic solar cells. So, many co-workers are working to search an efficient low cost device which has ability to fulfill both conditions as low production cost and higher conversion efficiencies. In this concerned, DSSC's have been attracting a lot of interest due to their high-energy conversion efficiency and low production cost. In 1991, the highest certified efficiency value reported by Gratzel was more than 11%. But, thereafter; none of the remarkable improved in efficiencies is not reported for DSSC devices. Also, DSSC suffering from some additional problems like dyes degradation in UV light and life of PV cells, cost of the high efficient metal complex dyes. Hence, there is prevailing need to search for low cost new materials synthesized by low cost chemical techniques and use these materials to construct the solar cell. In 1996, Könenkamp have put forward the idea of ETA solar cell concept, which has an ability to overcome the problems faced by DSSC. ETA cell works on the similar principle of DSSC but monolayer of dye is replaced by extremely thin film of inorganic metal chalcogenide absorber layer consisting of nanoparticles or quantum dots (QD's). The

semiconducting inorganic materials (CdS, CdSe, Bi₂S₃ and Sb₂S₃) are more stable than dye molecules. Also one can tune their electrical and optical properties according to their size.

Major reports are available for the synthesis of extremely thin film consisting of nanoparticles solar cells by using linker assisted chemical route. Where, colloidal nanoparticles have been synthesized in organic media. The TOP (trioctyl phosphine) and TOPO (trioctyl phosphine oxide) are frequently used as stabilizing ligands as they can coordinate both metal and chalcogen elements (S, Se, Te) and controls the nucleation, growth and avoids precipitation of semiconducting nanoparticles in chemical bath. The pre-synthesized capped semiconducting nanoparticles then attached on the surface of MO's for extremely thin film consisting of nanoparticles for solar cell application. The bifunctional linker/ligand molecules are chain of organic molecules influence on the charge transportation (increase the path of electron, hence losses are more) in the device also organic medium may be hazardous for high surface area of MO's. This is main reason to restrict the efficiencies of such devices [111-118].

Hence, the proposed research work is attributed to the synthesis of narrow band gap semiconducting nanoparticles onto wide band gap semiconducting MO (TiO₂). Efforts have been focused to synthesize quantum dots (size < 10 nm) to nano size of sensitizer materials and tune their size dependent properties by varying deposition parameters in thin absorber layers by using simple and low cost chemical techniques, their characterization and utilization for development of device grade solar cells. As mentioned in section 1.4, the extremely thin absorber layer consisting of nanoparticles consist of two sections 1) synthesis of porous nanostructure layer leading to high surface area fabricated from TiO₂ by low cost spin coating technique. 2) synthesis of extremely thin absorber layer consisting of nanoparticles of narrow band gap metal chalcogenides (CdS, CdSe, Bi₂S₃ and Sb₂S₃) by low cost wet chemical techniques without using linker/ligand molecules on the surface of the TiO₂.

Due to the importance of the MO electrode to provide the high internal surface area in the extremely thin absorber layer consisting of nanoparticles solar cells. Initially, the highly porous network TiO₂ was synthesized on FTO coated glass substrate by using spin coating techniques followed by sintering at high temperature (450°C) to increase electrical connectivity within the film. This provides high surface

area for the growth of sensitizer materials and act as window layer for the optical path.

The fabrication of sensitizer material on the entire surface of TiO₂ electrode has a prime importance. In practices, it is a very difficult to coat the TiO₂ surface by sensitizer without blocking any pores of TiO₂ network from top to bottom of TiO₂ film. Here, we made emphasis on the wet chemical synthesis route namely, chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR). Number of reports are available for the synthesis of individual inorganic (narrow band gap) semiconductor material with various morphologies but not reported for the layer heterostructures. By controlling the nucleation and growth kinetics to avoid precipitation in the reaction, the blocking of the porous network of TiO₂ can be avoided and it is difficult task without using linker/ligand molecules. However, in the present investigation, we have used simple wet chemical synthesis route and successfully deposited quantum to nano size particles of sensitizer material onto surface of TiO₂ nanoparticles without using linker/ligand molecules and by controlling the reaction kinetics such as concentration, deposition time, number of immersions, solvent and complexing agent. Here, the current investigation is based on the synthesis quantum to nano particles of CdS, CdSe, Bi₂S₃ and Sb₂S₃ as the extremely thin absorber layer consisting of nanoparticles onto porous TiO₂ at room temperature.

The synthesized layer heterostructures were used as a photoanode in extremely thin film consisting of nanoparticles for solar cell application. Hence, the layer structured TiO₂ and thin absorber layer films were characterized by different characterization techniques as follows

- **Structural studies by X-ray diffraction (XRD):** To confirm TiO₂ and metal chalcogenide layer, its phase and to know the crystallinity and orientation of the TiO₂ and thin absorber layer.
- **Surface morphology by scanning electron microscopy (SEM):** To observe the surface morphology of deposited material as high surface area is required for ETA solar cell along with interconnection of nanoparticles.
- **Optical absorption by UV-Vis-NIR spectrophotometer:** To check the absorption and band edge tuning of metal chalcogenide films with respect to change in particle size.

- **High resolution transmission microscopy (HR-TEM):** To check coating morphology and structure of metal chalcogenides onto TiO₂.
- **Energy dispersive and analysis spectroscopy (EDS):** To confirm the composition of desired material in the layer heterostructure.

Requirements for the construction of device grade extremely thin film consisting of nanoparticles solar cells:

- **Substrate:** Transparent conducting oxide (TCO) coated glass is used as substrates [fluorine doped tin oxide (FTO)].
- **Metal oxide semiconductor:** Wide band gap n-type semiconductor (TiO₂) having porous structure leading to high surface area for adsorption of extremely thin absorbing layer consisting of nanoparticles with appropriate thickness.
- **Photo-sensitizer (extremely thin film absorber layer consisting of nanoparticles):** The metal chalcogenide layer employed as extremely thin film solar cell has to meet several requirements should be sensitive to light (photosensitive), can absorb a broader range of the visible spectrum of light, the conduction band edge position is higher than TiO₂ (i.e. more electronegative), should be stable in redox couple electrolyte.
- **Hole conductor (Liquid Electrolyte):** It must be able to transfer holes from the sensitizer after the sensitizer has injected electrons in the porous semiconductor. The redox couple of S²⁻/S²⁻ (polysulphide) is usually used as an liquid electrolyte which can servers as an hole conducting media.
- **Back Contacts:** Platinum coated TCO is generally used as a back contact.

In order to develop layer heterostructure of TiO₂ and metal chalcogenides for photovoltaic application, we optimized the mesoporous TiO₂ thin film leading to high surface area for the adsorption of extremely thin film consisting of nanoparticles. Synthesized nanostructured then characterized by various characterization techniques. Finally, CdS, CdSe, Bi₂S₃ and Sb₂S₃ materials were coated on mesoporous TiO₂ thin film by using wet chemical synthesis techniques. The synthesized layer heterostructures used as photoanode in sandwich type photovoltaic cells. The constructed device performances were checked to get real sense of working solar cell device.