

**DEVELOPMENT OF NANOSTRUCTURED MATERIALS
FOR SOLAR CELL APPLICATIONS**



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MSPhD-MS-E-01
(MS Session: 2008-2010)

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A Thesis submitted to
Department of Materials Engineering,
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE (MS)
In
MATERIALS AND SURFACE ENGINEERING

SCHOOL OF CHEMICAL AND MATERIALS ENGINEERING
(SCME),
NATIONAL UNIVERSITY OF SCIENCES AND TECHNOLOGY
(NUST)
H-12, ISLAMABAD, PAKISTAN

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

AL-QURAN

*“You shall not accept any information,
unless you verify it for yourself.
I have given you the hearing,
the eyesight,
and the brain,
and you are responsible for using
them.”
(17: 36)*



AL-HADEES

*If you put your whole trust
in Allah,
as you ought,
He most certainly will
satisfy your needs,
as He satisfies those of the birds.
They come out hungry
in the morning,
but return full to their nests.
(Tirmidhi)*



DEDICATION

*Dedicated to my Family,
Which is my Life,
And to my Teachers,
Who are my Inspiration..*

ACKNOWLEDGEMENT

All praises are due to Almighty Allah, the Creator and Sustainer of the universe. He is the origin of all the knowledge and wisdom. Without his will nothing could be happened, Who enabled me to carry out this valuable work. All the regards to Holy Prophet Hazrat Muhammad (S. A. W.), Who paved our way towards success with the essence of faith in Allah and Who is forever an ivory tower for all of us.

I wish to express my deep gratitude and appreciation to my respected supervisor Dr. Mohammad Mujahid for his inspiring guidance, constant encouragement and fruitful discussions during the course of work. I would always look up to him as my guiding star and mentor. I am greatly indebted to my co-supervisor Dr. Mohammad Islam for his motivating suggestions and guidance during the research. I consider myself to be very fortunate and privileged to have worked under their guidance and supervision.

I greatly acknowledge Engr Fazal Elahi and Engr Salman Absar Director General SCME for providing a platform to utilize my skills in the research work. It is my pleasure to appreciate and thank Dr. Mohammad Bilal Khan Dean, SCME for his inspiring way of teaching and guiding. I feel honour to acknowledge Dr. K. Sanaullah (ex.HoD-CE) and Dr. A. Q. Malik Head of Chemical Engineering Department for providing the laboratory facilities. I would also like to thank all the faculty members, non teaching staff and my fellow students for the help provided to me at the various stages.

My deep appreciation and a bundle of thanks, for Dr. Umair Manzoor (Asst. Prof. Deptt. Of Physics) of COMSATS for his sincere and inspiring guidance and for the technical assistance specially in the making and testing of the dye sensitized solar cell.

I acknowledge Dr. Chen Zhong greatly for collaboration with our PV project. The intellectual and technical exchange with National Technological University, Singapore would greatly help to develop the project further.

I acknowledge. School of Civil and Environmental Engineering (SCEE), NUST, Pakistan Institute of Engineering and Applied Sciences (PIEAS) and AMtech lab. Rawalpindi, for the technical assistance provided during my research

At this stage I would like to remember and acknowledge my school and college teachers specially Mrs. Rubina Masud for making my base for learning the scientific knowledge and Mrs. Samera Mufaz who has always been there for me whenever I needed.

Finally my warmest appreciation and deepest gift of gratitude is for my Parents, who enabled me to follow my dreams and to find the best in myself and for their constant encouragement and limitless prayers. For my brother, sisters and sister in law for their constant support, care and prayers. Their belief in me has made me what I am today. I wish to fulfil their expectations

Sofia Javed.

CONTENTS

Acknowledgement.....	v
Contents.....	vii
List of figures.....	x
List of tables.....	xii
Abstract.....	xiii

CHAPTER 1

OVERVIEW OF PHOTOVOLTAICS.....1

1.1. The Need for Renewable Energy.....	1
1.2. Renewable Energy Resources.....	1
1.3. Solar Energy.....	2
1.3.1. Electricity generation from solar energy.....	2
1.3.1.1. Thermal Generation.....	2
1.3.1.2. Photovoltaics.....	3
1.4. Photovoltaics.....	3
1.4.1. History.....	3
1.4.2. Physics of Photovoltaics.....	4
1.4.3. Different Solar Cell Generations.....	5
1.4.3.1. First Generation Solar Cells.....	5
1.4.3.2. Second Generation Solar Cells.....	7
1.4.3.3. Third Generation Solar Cells.....	9
1.4.4. Applications of Solar Cells.....	13
1.4.5. Advantages.....	13
1.4.6. Disadvantages.....	14
1.5. Photovoltaics and Pakistan.....	14

CHAPTER 2

DYE SENSITIZED SOLAR CELLS.....16

2.1. Third Generation Solar Cells.....	16
2.2. Dye Sensitized Solar Cells.....	16
2.1.1. Configuration of DSSC.....	16

2.1.2. Working Principles.....	17
2.1.3. Factors Affecting Cell Performance.....	18
2.1.4. Efficiency of DSSC.....	19
2.1.5. Advantages and Disadvantages.....	19
2.1.6. Fabrication of DSSC.....	21
2.1.6.1. Synthesis of Titania Nanoparticles.....	21
2.1.6.2. Film Preparation.....	22
2.1.6.3. Processing of Titania Films.....	22
2.1.6.4. Assembling of DSSC.....	22
2.1.7. The Most Efficient DSSC to Date.....	22
2.1.8. Recent Developments in the Field of DSSC.....	23
2.2. Objectives.....	27

CHAPTER 3

MATERIALS AND METHODS.....28

3.1. Synthesis of Titania Nanoparticles.....	28
3.1.1. Preliminary Analysis.....	31
3.1.2. XRD Analysis.....	31
3.1.3. Scanning Electron Microscopy (SEM).....	31
3.2. Paste for Thin Films of Titania Nanoparticles.....	31
3.3. Deposition of Films by Doctor Blading.....	32
3.3.1. TGA/DSC Analysis.....	32
3.3.2. Optical Microscopy.....	32
3.3.3. SEM and EDS Analysis.....	32
3.3.4. Surface Area Measurement	32
3.4. Monolayer of N3 Dye over Titania Film.....	32
3.5. Making of Counter Electrode for DSSC.....	33
3.6. Assembling DSSC.....	33
3.7. Testing of the Cell.....	33
3.8. Sputter Coated Aluminium Film Over TCO Coated Glass.....	33
3.8.1. Physical Appearance.....	33
3.8.2. XRD Analysis.....	33
3.8.3. SEM and EDS.....	34

CHAPTER 4

RESULTS AND DISCUSSION.....35

4.1. Synthesis of Titania Nanoparticles.....	35
4.1.1. Mechanism of Sol Gel Synthesis.....	35
4.1.2. Preliminary Analysis.....	37
4.1.3. XRD Analysis.....	37.
4.1.4. Scanning Electron Microscopy.....	39
4.2. Paste for Thin Film of Titania Nanoparticles.....	46
4.3. Thin Films by Doctor blading.....	46
4.3.1. TGA/DSC Analysis.....	46
4.3.2. Optical Microscopy.....	48
4.3.3. SEM and EDS Analysis.....	50
4.3.4. Surface Area Measurement.....	53
4.4. Monolayer Deposition of N3 Dye Over Titania Films.....	54
4.5. Counter Electrode for DSSC.....	54
4.6. Assembling and testing of a Prototype DSSC.....	55
4.7. Aluminium Films.....	56
4.8.1. Physical Appearance	56
4.8.2. XRD Analysis.....	56
4.8.3. SEM and EDS Results.....	57

CHAPTER 5

CONCLUSIONS.....60

CHAPTER 6

FUTURE RECOMMENDATIONS.....62

6.1. Synthesis of Nanoparticles.....	62
6.2. Sintered Films.....	62
6.3. Production of 1-D Nanostructures.....	63
6.4. Columnar Aluminium Films.....	63
6.4. Making DSSC.....	63

BIBLIOGRAPHY.....65

List of Figures

CHAPTER 1

OVERVIEW OF PHOTOVOLTAICS

Figure 1.1: Basic construction of PV cell.....	4
Figure 1.2: Crystalline Si solar cell construction	6
Figure 1.3: Gallium Arsenide Solar Cell.....	6
Figure 1.4: Structure of amorphous Silicon.....	7
Figure 1.5: Amorphous Silicon Solar Cell.....	8
Figure 1.6: Thin Film Solar Cells, CIGS solar cell.....	9
Figure 1.7: CdTe solar cell.....	9
Figure 1.8: Organic Solar Cells.....	11
Figure 1.9: Cross-sectional representations of multiple-junctions solar cells.....	12

CHAPTER 2

DYE SENSITIZED SOLAR CELLS

Figure 2.1: Configuration of DSSC.....	17
Figure 2.2: Working of DSSC.....	18
Figure 2.3: Schematic of a dye sensitized solar tube.....	24
Figure 2.4: DNA like DSSC.....	25
Figure 2.5: Nanowire covered nanotube bilayer and its use in DSSC.....	25
Figure 2.6: Picture and schematic of 3D-DSSC module.....	26

CHAPTER 3

MATERIALS AND METHODS

Figure 3.1: Flow sheet for titania nanoparticles synthesis (method 1).....	29
Figure 3.2: Flow sheet for titania nanoparticles synthesis (method 2).....	30

CHAPTER 4

RESULTS AND DISCUSSION

Figure 4.1. XRD plots for as synthesized samples.....	37
Figure 4.2: XRD plots of annealed samples.	38
Figure 4.3: Crystallite size vs reflux duration.....	39

Figure 4.4: SEM images of Tit 1 at different magnifications.....	40
Figure 4.5: EDS analysis of Tit 1.....	40
Figure 4.6: SEM images of Tit 2 at different magnifications.....	41
Figure 4.7: EDS analysis od Tit 2.....	42
Figure 4.8: SEM images of Tit 3 dispersion in acetyl acetone.....	43
Figure 4.9: EDS analysis of Tit 3.....	43
Figure 4.10: SEM images of Ta 1.....	44
Figure 4.11: EDS analysis of Ta 1.....	45
Figure 4.12: SEM images of Ta 2.....	45
Figure 4.13: EDS analysis of Ta 2.....	46
Figure 4.14: TG/DT Analysis for Tit 1p.....	47
Figure 4.15: TG/DT Analysis for Tit 2p.....	47
Figure 4.16: TG/DT Analysis fro Tit 3.....	48
Figure 4.17: Optical microscope image of Tit1 film at lowest magnification.....	48
Figure 4.18: Optical microscope image of Tit 2 film.....	49
Figure 4.19: Optical microscope images of Tit 3 film.....	49
Figure 4.20: Surface morphology of Tit 1 film.....	50
Figure 4.21: Tit 1 film thickness.....	50
Figure 4.22: SEM images of Tit 2 film.....	51
Figure 4.23: EDS analysis of Tit 2 Film.....	51
Figure 4.24: SEM images of Tit 3 Film.....	52
Figure 4.25: EDS analysis of Tit 3 Film.....	53
Figure 4.26: Surface area vs refluxing time.....	54
Figure 4.27: Tit 3 film before and after dye uptake.....	54
Figure 4.28: Gold coated counter electrode for the DSSC.....	55
Figure 4.29: Assembled DSSC.....	55
Figure 4.30: Testing of DSSC.....	56
Figure 4.31: XRD pattern of Al Film.....	57
Figure 4.32: Peak matching of Al film XRD patterns.....	57
Figure 4.33: EDS analysis of Al Film.....	58
Figure 4.34: SEM images of Al film.....	58

List of Tables

CHAPTER 1

OVERVIEW OF PHOTOVOLTAICS

Table 1.1: Summary of confirmed, selected thin film solar cell efficiencies and related parameters, under standard measurement and reported conditions.....	10
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CHAPTER 3

MATERIALS AND METHODS

Table 3.1: Refluxing time for samples Tit 1, Tit 2, Tit 3.....	29
Table 3.2: Refluxing time for samples Ta 1, Ta 2.....	30

CHAPTER 4

RESULTS AND DISCUSSION

Table 4.1 : Designation of samples.....	36
Table 4.2. Crystallite size of Tit 1, 2 and 3 and Ta 1 and 2.....	38
Table 4.3: Surface area values of Tit 1, Tit 2 and Tit 3.....	53

ABSTRACT

The present work is based on the synthesis of nanostructures of wide band gap semiconductor material “titania” using sol gel refluxing method for the application in dye sensitized solar cells (DSSC). The precursor Titanium Tetraisopropoxide (TTIP) was modified by acetic acid giving Titanium Acetato Tris Isopropoxide (TATIP) and acetyl acetone giving Titanium Acetylacetonato Tris Isopropoxide (TAATIP). The effect of refluxing time (24 hrs (Tit 1, Ta 1), 70 hrs (Tit 2, Ta 2) and 120 hrs (Tit 3)) as well as precursor modifier on synthesis of titania was studied. The characterized nanoparticles were then used to make sintered films over TCO coated glass to make photoanode of DSSC. The characterization was performed using XRD, surface area measurement by BET method, TGA/DTA and SEM. Anatase phase is predominant in all the samples. The particle size range in annealed films is from 50 to 70 nm. In Tit 1 film there are about 500 nm sized spongy particles having around 50 nm sized pores. In Tit 2 although the particle size is in the same 50 nm range but they are clustered showing poor porosity and low surface area, in Tit 3 there are well dispersed particles of diameter around 50 nm. The film has high porosity and also there is proper connectivity between the particles to allow the efficient charge flow if used as photoanode. The best results were obtained from nanoparticles prepared by acetic acid modification and refluxing time of 120 hours (Tit 3), also the film obtained from Tit 1 (24 hr reflux) offers good porosity and linking among the particles but it is not so continuous at micro and macro level. The film from Tit 3 was then used to make a prototype DSSC and its testing was performed.

CHAPTER 1

OVERVIEW OF PHOTOVOLTAICS

1.1. THE NEED OF RENEWABLE ENERGY:

Energy is the backbone of today's society. It is vital for transportation, manufacturing, communication and many other elements that support our complex lives. The major use of energy is from its electrical form, which provides us with everything from heat for our homes to power for our appliances, communications and computational capabilities. Thus electricity and energy allow us to run our modern society.

We use natural energy resources to obtain heat and electricity. An energy resource is a source from which or a method by which energy can be obtained¹. For sustenance of earth, nature has provided energy in the form of various resources. Some of which are non-renewable and others are renewable.

Average Global electric power consumption is 15 TW.¹ Our major source of energy is non renewable i.e. almost 80% of the energy used worldwide is obtained from fossil fuels, including oil, coal and natural gas, solar energy in the form of biomass and hydropower supplies about 15%, and nuclear energy supplies about 5%. Geothermal energy, tidal power, and forms of solar energy other than biomass or hydropower together make up less than 1%². According to another source, in 2006, about 18% of global final energy consumption came from renewables.³

The supply of fossil fuels, a non-renewable energy resource, is limited and will run out some day. Besides harmful planetary or regional climatic changes including more severe natural catastrophes, such as hurricanes, droughts, flood etc^{4,5} are mainly the consequences of use of fossil fuels as primary energy resource.

Due to these reasons there is propensity worldwide to utilize renewable and benign energy resources to meet immense energy needs.

1.2. RENEWABLE ENERGY RESOURCES

Renewable energy is derived from natural processes that are replenished constantly. In its various forms, it derives directly or indirectly from the sun, or from heat generated

deep within the earth. Included in the definition is electricity and heat generated from solar, wind, ocean, hydropower, biomass, geothermal resources, and biofuels and hydrogen derived from renewable resources.⁶

The harness of energy from all renewable resources other than solar need costly equipment, huge land area, are accompanied with undesirable ecological variations or the sources are located at isolated far away places. But solar energy is the one which is unlimited and available everywhere besides it offers cheaper harness options. So lets emphasize on solar energy and the ways in which we can gather energy from sun.

1.3. SOLAR ENERGY:

Solar energy comes from the nuclear fusion power from the Sun. The sun, an average star, is a fusion reactor that has been burning over 4 billion years and provides incredible amounts of energy. It can supply the world's energy needs for one year in just one hour. It is also a fact that, "The amount of solar radiation striking the earth over a three-day period is equivalent to the energy stored in all fossil energy sources."⁷

This energy can be collected and utilised in a few different ways⁸.

- Generate electricity using photovoltaic solar cells.
- Generate electricity by heating trapped air which rotates turbines in a solar updraft tower.
- Generate hydrogen using photoelectrochemical cells.
- Heat water or air for domestic hot water and space heating needs using solar-thermal panels.
- Heat buildings, directly, through passive solar building design.
- Heat foodstuffs, through solar ovens.
- Solar air conditioning

1.3.1. Electricity generation from solar energy:

From solar power electricity can be generated in two ways thermal and photovoltaic.

1.3.1.1. THERMAL GENERATION:

Thermal generation of electricity from sun concentrates sunlight, converts it into heat, and applies it to a steam generator or engine to be converted into electricity in order to warm

buildings, heat water, generate electricity, dry crops or destroy dangerous waste. Electricity is generated when the heated fluid drives turbines or other machinery⁷.

1.3.1.2. PHOTOVOLTAICS:

Photovoltaics or solar cells produce electricity directly without any moving parts. Power is produced when sunlight strikes a semiconductor material and creates an electric current.

1.4. PHOTOVOLTAICS

Photovoltaics is the field of technology and research related to the application of semiconductor based solar cells for energy by converting solar energy (including ultra violet radiation) directly into electricity.⁹ These cells produce electricity by means of the photoelectric effect, i.e., the photons from sunlight are converted into electrical current^{9, 5}. Photovoltaic production has been doubling every 2 years, increasing by an average of 48 percent each year since 2002, making it the world's fastest-growing energy technology, and then increased by 110% in 2008¹⁰. At the end of 2008, the cumulative global PV installations reached 15,200 megawatts.^{11,12}

1.4.1. History:

The physical effect which underlies photovoltaics was first observed by Alexandre-Edmond Becquerel in 1839¹³, when he obtained a current by exposing silver electrodes to radiation in an electrolyte. In 1877 Adams and Day¹⁴ observed that the exposure of selenium electrodes to radiation produced an electric voltage, thus allowing them to produce electric current.

The effect was incomprehensible until the discovery of transistors and the explanation of the physics of the p-n junction by Shockley¹⁵ and Bardeen and Brattain¹⁶ in 1949, the year that marked the beginning of the semiconductor era. Then, in 1954 Chapin et al¹⁷ at the Bell Laboratories in USA developed the first solar cell based on crystalline silicon, which had an efficiency of 6%. This efficiency was increased to 10% within a few years. The first viable use for solar cells was in satellite power supplies. The main driving force behind the widespread use of photovoltaics for terrestrial power supplies came in 1973 with the notorious oil shock. From this point onwards numerous research and development institutions were set up around the world, the majority of which were publicly financed. All the available options for cost reduction were examined, as it was already recognised that the

excessive costs of photovoltaic plants posed the largest obstacle for their widespread use. While most PV cells in use today are silicon-based, cells made of other semiconductor materials are expected to surpass silicon PV cells in performance and cost and become viable competitors in the PV marketplace.

1.4.2. Physics of photovoltaics:

The physics of the PV cell is very similar to the classical p-n junction diode. When light is absorbed by the junction, the energy of the absorbed photons is transferred to the electron system of the material, resulting in the creation of charge carriers that are separated at the junction. The charge carriers may be electron-ion pairs in a liquid electrolyte or electron hole pairs in a solid semiconducting material. The charge carriers in the junction region create a potential gradient, get accelerated under the electric field and circulate as the current through an external circuit. The current squared times the resistance of the circuit is the power converted into electricity. The remaining power of the photon elevates the temperature of the cell.

The origin of the photovoltaic potential is the difference in the chemical potential, called the Fermi level, of the electrons in the two isolated materials. When they are joined, the junction approaches a new thermodynamic equilibrium. Such equilibrium can be achieved only when the Fermi level is equal in the two materials. This occurs by the flow of electrons from one material to the other until a voltage difference is established between the two materials which have the potential just equal to the initial difference of the Fermi level. This potential drives the photocurrent.^{18, 19}

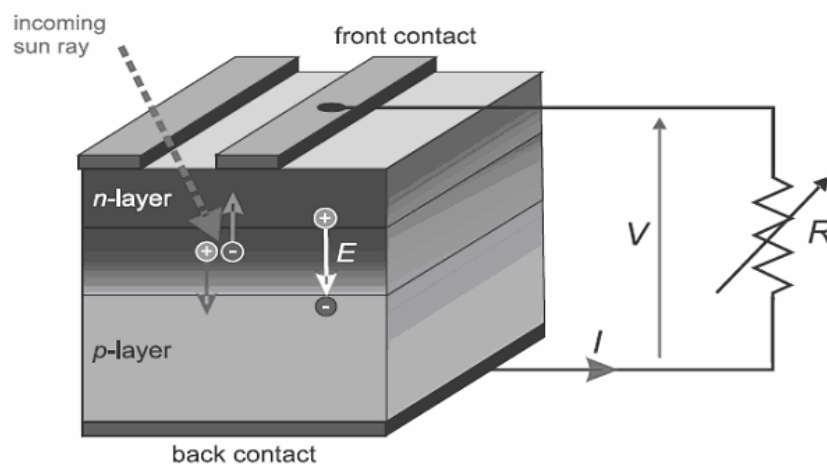


Figure 1.1: Basic construction of PV cell

(Source: Solar Electric Power Generation-Photovoltaic Energy Systems, Krauter, Stefan C. W., Springer, 2006)

Figure 1.1 above shows the basic cell construction. For collecting the photocurrent, the metallic contacts are provided on both sides of the junction to collect electrical current induced by the impinging photons on one side. Conducting foil contact is provided over the bottom surface (back contact) and on one edge of the top (illuminated) surface. Thin conducting mesh on the remaining top surface collects the current and lets the light through. The spacing of the conducting fibers in the mesh is a matter of compromise between maximizing the electrical conductance and minimizing the blockage of the light. In addition to the basic elements, several enhancement features can also be included in the construction. For example, the front face of the cell can have anti-reflective coating to absorb as much light as possible by minimizing the reflection. The mechanical protection is provided by the cover glass applied with a transparent adhesive.

1.4.3. Different solar cell generations:

There is a challenge to obtain maximum amount of electrical energy from the available solar energy and as a result of extensive research and development in this field this challenge is shifting towards production of devices with higher efficiencies and lower costs. Different types of materials, which vary from each other in terms of light absorption efficiency, energy conversion efficiency, manufacturing technology and cost of production, have been evolved for use in photovoltaics²⁰. Depending upon the material and period of its evolution the solar cell technology has been divided into three generations.

1.4.3.1. FIRST GENERATION SOLAR CELLS:

(i) Crystalline Silicon Solar Cell:

Crystalline silicon cells are the most common in the PV industry. Single-crystal silicon has a uniform molecular structure, its high uniformity results in higher energy conversion efficiency. The conversion efficiency for single-silicon commercial modules ranges between **15-20%**²¹. The record efficiency is 24.7%²².

There is a disadvantage that Si solar cells are costly. About half of the manufacturing cost comes from wafering to produce wafers with a thickness no less than 200 micrometers.

Construction and charge flow:

The bulk of the cell is formed by a thick p-type base where most of the incident light is absorbed and most power is generated. After light absorption, the minority carriers

(electrons) diffuse to the junction where they are swept across by the strong built-in electric field. The electrical power is collected by metal contacts to the front and back of the cell.

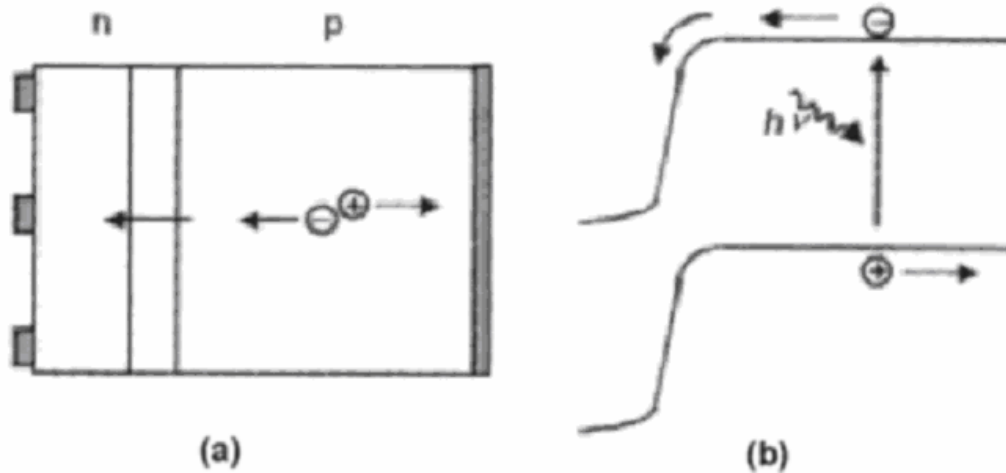


Figure 1.2: crystalline Si solar cell construction, (a) physical construction, (b) energy levels.

(Source: Solar Cells, Materials, Manufacture and Operation edited by Tom Markvart and Luis Cataner, Elsevier, 2005)

(ii) Gallium Arsenide Solar Cell:

The structure of GaAs is similar to that of silicon but relative to Si it has got a high level of light absorptivity. Also, GaAs has much higher energy conversion efficiency than crystal silicon, reaching about 25 to 30%.²³ Its high resistance to heat makes it an ideal choice for concentrator systems in which cell temperatures are high. Strong resistance to radiation damage and high cell efficiency make GaAs solar cells popular in space applications.

The biggest drawback of GaAs PV cells is the high cost of the single-crystal substrate that GaAs is grown on. Therefore it is most often used in concentrator systems where only a small area of GaAs cells is needed.²³

Construction and charge flow:

Figure 1.3 depicts the working of this kind of cell. The typical gallium arsenide solar

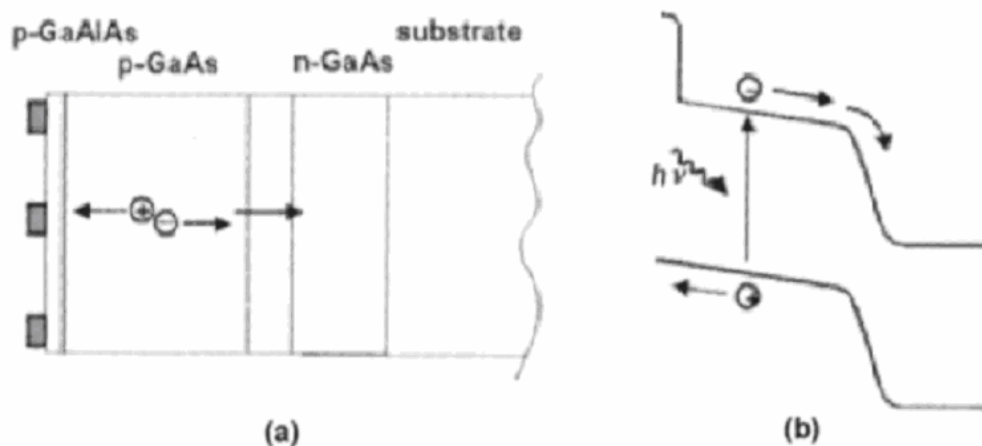


Figure 1.3: Gallium Arsenide Solar Cell, (a) physical construction, (b) energy levels.

(Source: Solar Cells, Materials, Manufacture and Operation edited by Tom Markvart and Luis Cataner, Elsevier, 2005)

cell is a heterojunction structure, by virtue of the thin passivating GaAlAs layer which covers the top surface. The GaAlAs 'window' layer prevents minority carriers (electrons) from the emitter to reach the surface and recombine but transmits most of the incident light into the emitter layer where most of the power is generated.

1.4.3.2. SECOND GENERATION SOLAR CELLS:

(i) Amorphous Silicon Solar Cells:

The atomic structure of amorphous silicone is shown in figure 1.4. The band gap of this semiconductor is approximately 1.7 eV, but varies between certain limits due to the hydrogen content^{24, 25}. Only a thin layer of a-Si is sufficient for making PV cells (about 1 micrometer thick). a-Si still has two major roadblocks to overcome. One is the low cell energy conversion efficiency, ranging between 5-9%, and the other is the outdoor reliability problem in which the devices could lose 50% or more of their power output over the first hundreds of hours of exposure to light²⁶. However, research and development has resulted in achievement of **13%** efficiency²⁷.

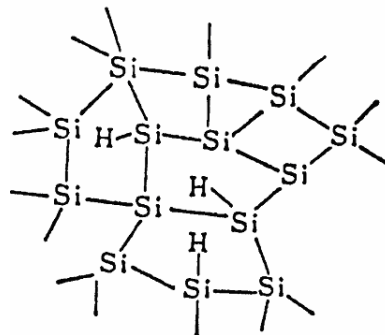


Figure 1.4: Structure of amorphous Silicone
(Source: Crystalline Silicone Solar Cells by Adolf Goetzberger, Joachim Knobloch, Bernhard Vob, John Wiley and Sons 1998)

Construction and working:

The structure of single-junction amorphous silicon solar cells is shown below (Fig 1.5). Based on p-i-n junction, this cell contains a layer of intrinsic semiconductor which separates two heavily doped p and n regions near the contacts. Generation of electrons and holes occurs principally within the space-charge region, with the advantage that charge separation can be assisted by the built-in electric field, thus enhancing the collection efficiency. The contacts are usually formed by a transparent conducting oxide (TCO), at the top of the cell, and a metal contact at the back. Light trapping features in TCO can help

reduce the thickness and reduce degradation. The thickness of a-Si solar cells ranges typically from a fraction of a micrometer to several micrometers.

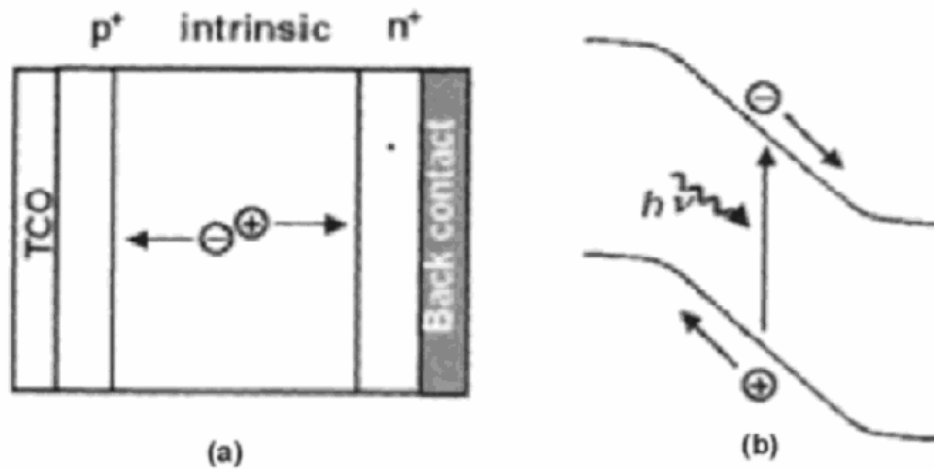


Figure 1.5: Amorphous Silicon Solar Cell, a) physical construction, (b) energy levels.

(Source: Solar Cells, Materials, Manufacture and Operation edited by Tom Markvart and Luis Cataner, Elsevier, 2005)

(ii) Cadmium Telluride and CIGS:

a) Cadmium Telluride:

As a polycrystalline semiconductor compound made of cadmium and tellurium, CdTe has a high light absorptivity level that only about a micrometer thick film can absorb 90% of the solar spectrum²¹. Another advantage is that it is relatively easy and cheap to manufacture by processes such as high-rate evaporation, spraying or screen printing. The best laboratory cells have achieved efficiencies of 10-14%^{28,29}. The instability of cell and module performance is one of the major drawbacks of using CdTe for PV cells. Another disadvantage is that cadmium is a toxic substance. Although very little cadmium is used in CdTe modules, extra precautions have to be taken in manufacturing process.

b) CIGS:

Polycrystalline semiconductor compounds of copper, indium gallium and selenium, CIS and CIGS represent major research areas in the thin film industry. CIS has the highest “research” energy conversion efficiency of 17.7% in 1996, and 19.5% in 2004. CIS and related alloys offer a class of the most light-absorbent semiconductors 0.5 micrometers can absorb up to 90% of the solar spectrum.

CIS is an efficient but complex material. Its complexity makes it difficult to manufacture. Also, safety issues might be another concern in the manufacturing process as it involves hydrogen selenide, an extremely toxic gas.²³

Construction and working:

The basic structures of solar cells based on compound semiconductors copper indium-gallium diselenide (a, b) and cadmium telluride (c, d) are shown below. The front part of the junction is formed by a wide band gap material (CdS 'window') which transmits most of the incident light to the absorber layer (Cu (In, Ga) Se₂ or CdTe) where virtually all electron-hole pairs are produced. The top contact is formed by a transparent conducting oxide.

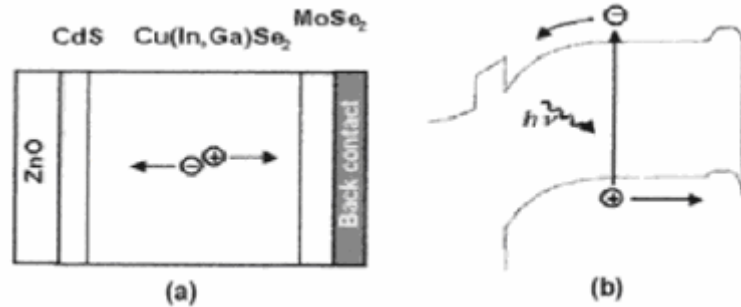


Figure 1.6: Thin Film Solar Cells, CIGS solar cell, (a) physical construction, (b) energy levels
(Source: Solar Cells, Materials, Manufacture and Operation edited by Tom Markvart and Luis Cataner, Elsevier, 2005)

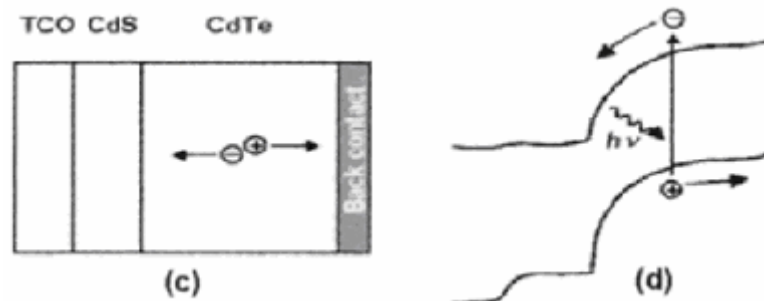


Figure 1.7: CdTe solar cell, (c) physical construction, (d) energy levels.

(Source: Solar Cells, Materials, Manufacture and Operation edited by Tom Markvart and Luis Cataner, Elsevier, 2005)

1.4.3.3. THIRD GENERATION SOLAR CELLS:

The third generation solar cell technologies investigate photovoltaic conversion schemes with the potential to reach efficiencies substantially higher than the theoretical efficiency limit for traditional single-junction devices 31%. This generation is more or less in the research phase yet. Without going into the details, some of the approaches that come under this generation are: hybrid solar cells (organic solar cells, dye sensitized solar cells),

V_{oc} (mV)	J_{sc} (mA/cm ²)	Area (cm ²)	Efficiency (%)	Organization	Comments
Cu-ternary and multinarys					
678	32.5	0.449	18.8	NREL	ZnO/CdS/CIGS (12/98); also, 18.2%, 1.1 cm ² cell (1/99)
693	35.7	0.410	19.5	NREL	ZnO/CdS/CIGS (9/04)
669	35.73	1.039	18.4	NREL	Large area (3/01)
605	36.19	0.462	15.0	NREL	ZnO/CIGS(1/99) Cd-free cell
666	30.51	0.418	15.4	NREL	ZnO/CdS/CIGS (electrodeposited) (2/99)
636	34.64	0.442	15.7	NREL	ZnO/[Cd-doped CIGS] (2/01)
671	34.0	0.15 (Active area)	17.7 17.4	Ritsumeikan University NREL	Active area efficiency; ZnS buffer, small area (11/00) CIGS on stainless steel (flexible) 2/00
539	33.7	0.192	13.4	Siemens Solar	ZnO/CdS/CIS (11/92)
736	510.1	0.102	21.1	NREL	Concentrator: 14.3× (21.5% direct, 14.1× (3/01)
CdTe					
843	25.09	1.047	15.8 15.8	Univ. South Florida NREL	MgF ₂ /7059 glass/SnO ₂ /CdS/CdTe/C/Ag (6/92) MgF ₂ /7059 glass/SnO ₂ /CdS/CdTe/glass (4/99)
848	25.86	1.131	16.4	NREL	CdSnO/CdS/CdTe/ glass (2/01)
845	25.90	1.132	16.5	NREL	CdSnO/CdS/CdTe/ glass (9/01)
840	26.1	1.0	16.0	Matsushita	3–5 μm CSS CdTe; question QE-current (3/97)
Dye sensitized and organic solar cells					
795	19.4	0.25	11.0	EPFL	Nanocrystalline dye (Grätzel (12/96)
795	11.3	141.4	4.7	INAP	Nanocrystalline dye (Grätzel) submodule (2/98)
726	15.8	2.36	8.2	ECN	Nanocrystalline dye (Grätzel) (7/01)
522	22.7	4.00	7.8*	Toshiba	GLE (polymer gel electrolyte) Photoe-electrochemical cell (5/00)
835	6.3		3.3* 4.9	Bell Labs/Lucent NREL	"Plastic Cell" (ITA/Pentacene) (5/00) "Plastic Cell" (8/05)
Advance tandems					
		4.0	25.8	Kopin/Boeing	GaAs/CIS thin film (11/89)
		2.4	14.6	ARCO	a-Si:H/CIGS (6/88)
0.768	25.5	2.4	13.8	NREL	Transparent CdTe cell
0.357	6.06		1.47		CIS cell
1.14			15.3		Glass/Cd ₂ SnO ₄ /ZnSnO _x /CdS:O/CdTe/Cu _x Te—Glass/Mo/CIGS/CdS/ZnO CdTe/CIS 4-terminal mechanical stack (12/04)

Table 1.1: Summary of confirmed, selected thin-film solar-cell efficiencies and related parameters, under standard measurement and reporting conditions.²¹

multiple energy threshold process approach (multiple band and impurity solar cells), multiple electrons per incident photon, hot carrier solar cells³⁰ (quantum dot solar cells) and thermal affects approaches (thermophotonics etc.).

In third generation solar cells among others, the dye-sensitized solar cells (DSSC) have great potential to render solar energy as an economically attractive sustainable energy source. They offer so many advantages offer simple fabrication and assembling procedures and there is a big room to improve their efficiency. That's why only DSSC are emphasized here. Also tandem cells are touched briefly as the maximum efficiency to date is achieved for a tandem cell.

(i) Materials for Dye Sensitized Solar Cells:

The use of mesoporous nanocrystalline films of the semiconductor considerably increases the effective surface area for dye adsorption. For this reason recent studies of dye-

sensitized solar cells use invariably such nanocrystalline films. Amongst nano oxide semiconductors, titanium dioxide (TiO₂), a cheap and readily available white pigment, is the most commonly used, however others like zinc oxide³¹⁻³³ and tin oxide³⁴⁻³⁹ are also the candidate materials⁴⁰.

Materials for dyes in dye sensitized solar cells can involve transition metal complexes derived from polypyridines, porphine or phthalocyanine as ligands⁴¹⁻⁴⁷. The standard systems for polypyridines are mono- and polynuclear complexes based on Ru (II). For metalloporphyrins and metallophthalocyanines the preferred metal ions are those with full or half-filled d-shells such as Zn (II), Mg (II) or Al (III). Reactive groups like silanyl, carboxylic acid or phosphonic acid) react spontaneously with surface hydroxyl groups of oxide surfaces to form linkages that exhibit good stability.

The electrolyte is usually organic (generally a nitrile) containing a redox electrolyte I⁻/ I₃⁻.⁴⁰ An efficiency of 12.04% has been achieved so far.⁴⁸

Construction and working:

The most recent types of solar cell are based on molecular materials. In these cells, light is absorbed by a dye molecule, transferring an electron from the ground state to an excited state, rather than from the valence band to the conduction band, as in the semiconductor cells. The electron is subsequently removed to an electron

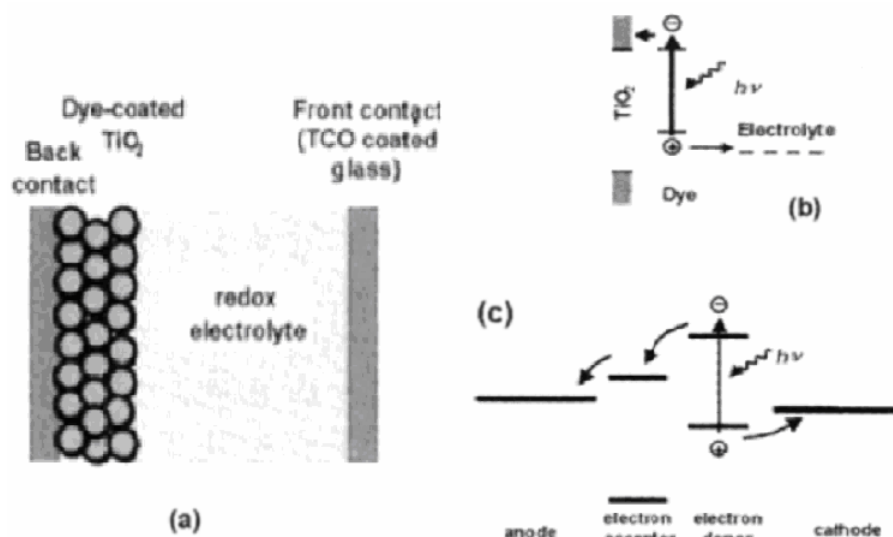


Figure 1.8: Organic Solar Cells, (a) physical construction, (b, c) energy level diagrams.

(Source: Solar Cells, Materials, Manufacture and Operation edited by Tom Markvart and Luis Cataner, Elsevier, 2005)

acceptor and the electron deficiency (hole) in the ground state is replenished from an electron donor. A number of choices exist for the electron acceptor and donor. In the dye sensitised cell the electron donor is a redox electrolyte and the role of electron acceptor is

the conduction band of titanium dioxide. In plastic solar cells both electron donor and electron acceptor are molecular materials.

(ii) Tandem solar cells:

The first laboratory demonstrations of multiple-junction devices with efficiency greater than 30% were actually reported at the beginning of the 1990s⁴⁹⁻⁵¹. Various 2, 3, and 4 terminal configurations, shown in Fig.10, have been investigated over last 20 years. These cells attain “beyond the conventional” efficiencies because they use multiple devices in the same area, each tuned to a different portion of the solar spectrum (e.g., the top cell tuned to the red and the bottom cell to the blue). Thus, the total device is more effective in utilizing the total frequencies of the sunlight that intercepts its surface. Three types of state-of-the-art III-V triple-junction solar cells have recently surpassed the 40% efficiency mark.⁵²⁻⁵⁴

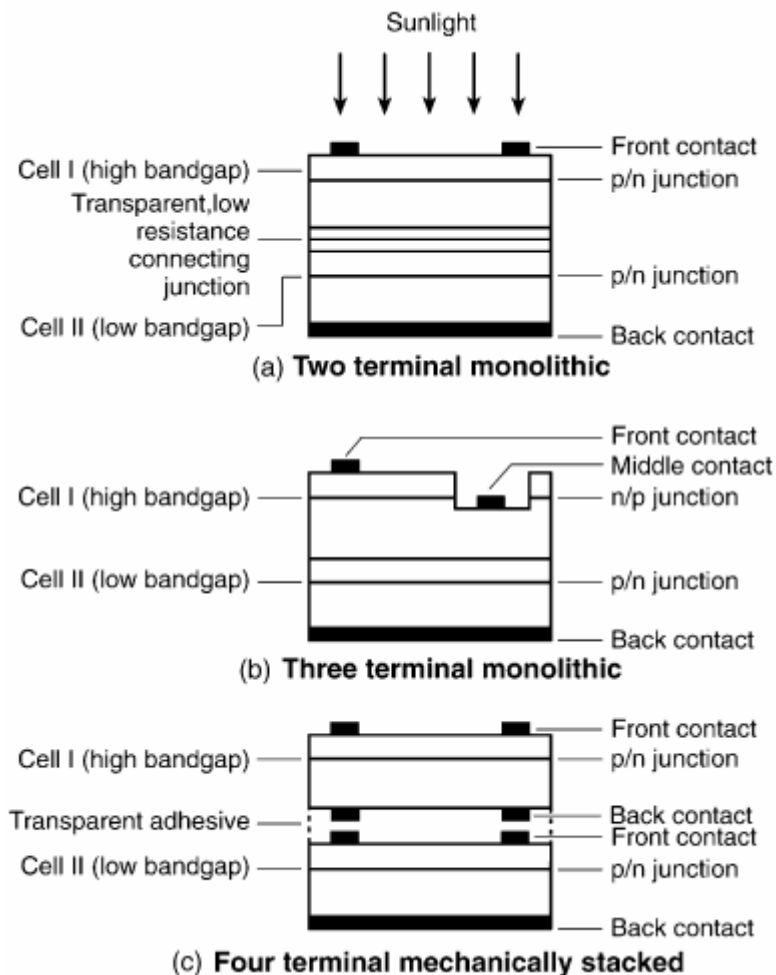


Figure 1.9: Cross-sectional representations of multiple-junctions solar cells, showing (a) 2-terminal monolithic, (b) 3-terminal monolithic, and (c) 4-terminal mechanically stacked configurations.

(Source: L.L. Kazmerski; Journal of Electron Spectroscopy and Related Phenomena 150 (2006) 105–135)

1.4.4. Applications of Solar Cells:

There are four broad categories that can be identified for solar energy use: industrial, rural habitation, grid-connected, and consumer/indoor. Industrial uses represent the largest applications of solar power in the past 30 years. Telecommunications, oil companies, and highway safety equipment all rely on solar power for dependable, constant power far from any power lines.⁷

Roadside call boxes and lighted highway signs rely on the sun's energy in order to provide reliable services without buried cable connections or diesel generators.

Navigational systems such as marine buoys and other unmanned installations in harsh remote areas are also ideal applications for solar power because "the load demands are well known and the requirements for reliable power are the highest."

Rural habitation includes "cabins, homes, villages, clinics, schools, farms, as well as individually powered lights and small appliances.

Grid-connected systems pair solar power with an existing grid network in order to supply a commercial site with enough energy to meet a high demand, or to supplement a family's household supply.

Consumer/indoor uses of PV cells include watches and calculators; PV modules power computers and radios.

1.4.5. Advantages:

Solar energy is a free, inexhaustible resource. There are several advantages of photovoltaic solar power that make it one of the most promising renewable energy sources in the world. It is non-polluting, has no moving parts that could break down, requires little maintenance and no supervision, and has a life of 20-30 years with low running costs. It is especially unique because no large-scale installation is required. Remote areas can easily produce their own supply of electricity by constructing as small or as large a system as needed. Photovoltaics are simply distributed to homes, schools, or businesses, where their assembly requires no extra development or land area and their function is safe and quiet. An average home has more than enough roof area to produce enough solar electricity to supply all of its power needs. With an off inverter, which converts direct current (DC) power from the solar cells to alternating current (AC), solar cells can run most home appliances. In this

way a solar home can look and operate very much like a home that is connected to a power line. Any excess electricity generated can be fed back to the electrical grid if connected.

As communities grow, more solar energy capacity can be added, thereby allowing power generation to keep in step with growing needs without having to overbuild generation capacity as is often the case with conventional large scale power systems.

Photovoltaic power has advantages over wind power, hydropower, and solar thermal power. The latter three require turbines with moving parts that are noisy and require maintenance. Also if we compare PV characteristics to those of coal, oil, gas, or nuclear power, the choice is easy. Solar energy technologies offer a clean, renewable and domestic energy source.

The practicality and environmentally safe nature of solar power is influencing people worldwide, which is evident in equipment sales. According to Siemens Solar, production of PV cells and modules increased threefold from 40 MW in 1990 to about 120 MW in 1998. Worldwide sales have been increasing at an average rate of about 15% every year during the last decade. There is a realistic possibility for the market to continue to grow at about a 15% rate into the next decade. At this rate, the world production capacity would be 1000 MW by 2010, and photovoltaics could be a \$5 billion industry.

1.4.6. Disadvantages:

There are only two primary disadvantages to using solar power: amount of sunlight and cost of equipment. The amount of sunlight a location receives varies greatly depending on geographical location, time of day, season and clouds. Globally, areas receiving very high solar intensities include developing nations in Asia, Africa and Latin America. A storage system can be used to have electricity during nights.

As the price of solar power lowers and that of conventional fuels rises, photovoltaics is entering a new era of growth and implementation. So much so, that solar power will remain an excellent energy option forever till life exists.

1.5. PHOTOVOLTAICS AND PAKISTAN:

The renewable energy potential is largely unutilised in Pakistan except hydrel power generation. The main reason behind this limited interest in renewable energy resources is the high costs associated with them. We are facing acute electricity shortages with increasing

energy demands and the nuisance of load shedding is poorly affecting the progress of our country. We desperately need a cheap and reliable energy alternative.

Photovoltaics can offer an utilisable energy alternative in the form of nanostructured dye sensitised solar cells as the materials are cheap like TiO_2 and the redox electrolyte. We can find out a cheap and environment friendly dye sensitizer out of so many material options (some are shown in table 2). The maximum efficiency obtained so far is 12.04%.⁴⁸ Even if these solar cells are not so efficient at energy conversion, for a country like ours where we obtain a plenty of sunlight throughout the year, we can overlook somehow the low efficiency for so many advantages²⁹ like:

- Low cost and ease of production
- Performance increases with temperature narrowing the efficiency gap
- Bifacial configuration
- Efficiency less sensitive to angle of incidence
- Transparency for power windows
- Colour can be varied by selection of the dye, invisible PV-cells based on near-IR sensitizers are feasible
- Payback time is only a few months as compared to years for silicon.
- Outperforms amorphous Si
- Flexibility
- Light weight
- Ease of integration

The other materials are less suitable for us. For example if we consider silicone and other crystalline III-V semiconductors they are too costly. Thin film cells offer less efficiency, the devices have complex structures, manufacturing is also complex and toxic by-products are formed.

Therefore it is justified and beneficial that we may work to develop nanostructured dye sensitized solar cells to help with the mounting energy demands of our country.

In the following chapter the various aspects of dye sensitized solar cells are briefly described.

CHAPTER 2

DYE SENSITIZED SOLAR CELLS

2.1. THIRD GENERATION SOLAR CELLS

Third generation photovoltaic cells, also called advanced thin-film photovoltaic cell, is a range of novel alternatives to "first generation" and "second generation" cells⁵⁵. These are based on the concepts that allow for a more efficient utilization of the sunlight⁵⁶.

The third generation solar cells include hybrid solar cells (organic solar cell and dye sensitized solar cell(DSSC)), multiple energy threshold device, tandem solar cells, multiple quantum well solar cells, impurity solar cells, cells utilizing up-conversion and down-conversion concepts, quantum dot solar cells and thermophotonics etc.⁵⁷⁻⁶³ Most of the concepts are still in theory building stage. However extensive research would make the third generation solar cells capable of achieving the desired goals in terms of low cost and high efficiency

Among third generation solar cells we are more interested in dye sensitized solar cells because these offer low cost with so many advantages, and already have achieved an efficiency of 10 %⁶⁴, their fabrication involves simple steps. A detailed description of this kind of solar cells is given below:

2.2. DYE SENSITIZED SOLAR CELLS:

The dye-sensitized solar cell is an interesting photochemical system in which a device is designed and molecularly engineered to perform light conversion into electricity. It is a fascinating multidisciplinary topic of current interest and a very active research field. It has attracted wide attention in the recent years. It also illustrates an application that has evolved from fundamental investigation to the concept of specifically designed artificial molecular devices.⁶⁵ These cells offer great potential for developing clean and economically sustainable energy sources.

2.2.1. Configuration of DSSC:

The device is constituted of two transparent conducting oxide substrates, TCO, such as fluorine doped tin oxide, FTO, on glass or polymeric substrates. One TCO is a photoanode, composed of a sensitizer adsorbed onto the surface of the nanocrystalline

semiconductor electrode (typically nanostructured TiO_2), and the other a photoinert counter electrode with a thin layer of a catalyst (for instance, platinum) sandwiching an electrolyte/relay medium (usually a solution containing the I^{3-}/I^- pair).⁶⁵

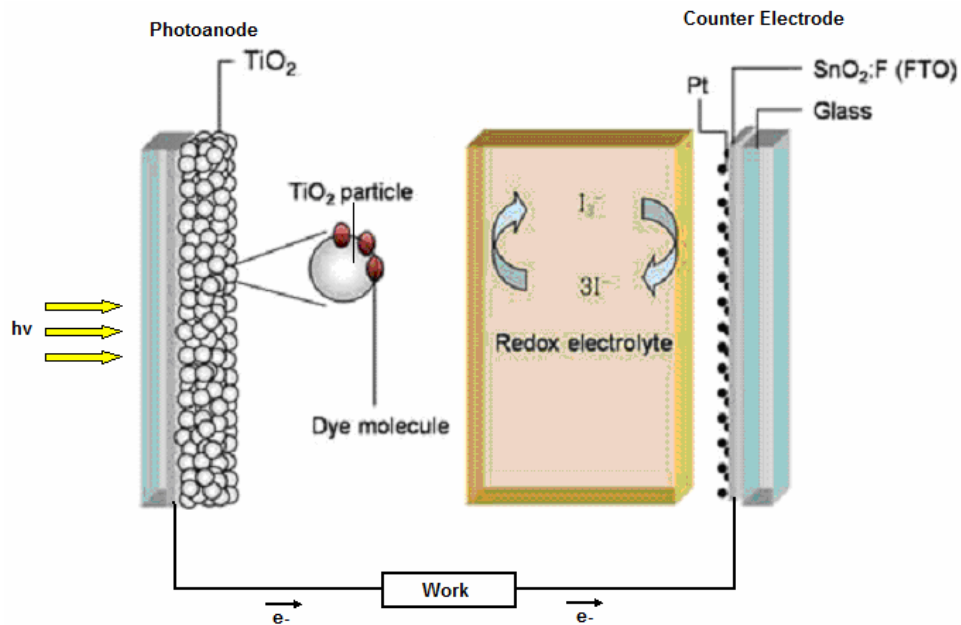


Figure 2.1: Configuration of DSSC

(Source: www.moleculardevices.se/ourresearch/workingprinciples.html)

2.2.2. Working Principles:

A schematic presentation of the operating principles of the DSC is given in fig 2.2. On the surface of the nanocrystalline film a monolayer of the charge transfer dye is deposited, whose photo excitation results in the injection of an electron into the conduction band of the semiconductor. The original state of the dye is subsequently restored by electron donation from the electrolyte, usually an organic solvent containing redox system, such as the iodide/triiodide couple. The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The iodide is regenerated in turn by the reduction of triiodide at the counter electrode. The circuit gets completed via electron migration through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte and is called the open circuit voltage⁶⁶.

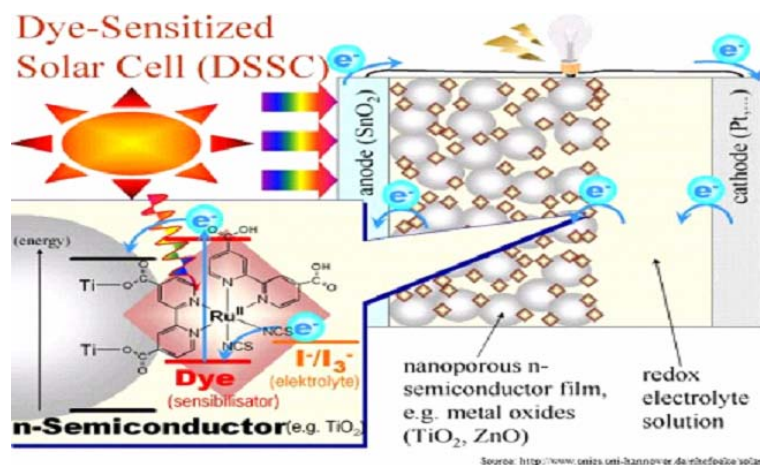


Figure 2.2: Working of DSSC

(Source: <http://www.unics.uni-hannover.de/nhcfoeke/solar>)

Overall the device generates electric power from light without suffering any permanent chemical transformation⁶⁶.

2.2.3. Factors Affecting Cell Performance:

In a multi-component device, the overall performance of the solar cell depends critically on the individual properties of the constituent components and processes.

- The structure, morphology, optical and electrical properties of the nanoporous oxide layer.
- Chemical, redox and photophysical and photochemical properties of the dye.
- Visco-elastic and electrical properties of the electrolyte carrying the redox mediator.
- Redox and optical properties of the redox mediator.
- Electrical and optical properties of the counter electrode.

Regarding key processes one can cite: light absorption, charge injection from the excited state of the dye; regeneration of the oxidized dye; electron percolation within the oxide film; dark currents and counter-electrode performance.

For devices targeted for commercialization, there are additional factors to consider such as: long term stability and material cost. Optimal performance is obtainable only when we can understand the factors that control each of these components and our ability to tune to the required configuration. On one hand with involvement of so many parameters, these

solar cells are extremely delicate devices to fabricate in a reproducible manner. On the other hand these parameters allow total flexibility in tuning to specific applications.⁶⁷

2.2.4. Efficiency of DSSC⁶⁷:

Quantitative assessment of the solar cell performance is given by two key parameters: the incident photon-to-current conversion efficiency (IPCE) for monochromatic radiation and overall white light-to-electrical conversion efficiency η_{eff} . The IPCE value is the ratio of the observed photocurrent divided by the incident photon flux, uncorrected for reflective losses during optical excitation through the conducting glass electrode:

$$\text{IPCE} = \frac{\text{No. of electrons flowing through the external circuit}}{\text{No. of incident photons}}$$

The IPCE value can be considered as the effective quantum yield of the device. It is the product of three key factors:

- Light harvesting efficiency LHE (λ) (depend on the spectral and photophysical properties of the dye),
- The charge injection yield ϕ_{inj} (depend on the excited state redox potential and the lifetime), and
- The charge collection efficiency η_{el} (depend on the structure and morphology of the TiO₂ layer)

$$\text{IPCE} = (\text{LHE}_\lambda) (\phi_{\text{inj}}) (\eta_{\text{el}})$$

The overall efficiency (η_{global}) of the photovoltaic cell can be obtained as a product of the integral photocurrent density (i_{ph}), the open-circuit photovoltage (V_{oc}), the fill factor (ff) and the intensity of the incident light (I_s):

$$\eta_{\text{global}} = \{i_{\text{ph}} V_{\text{oc}} \text{ff}\} / I_s$$

2.2.5. Advantages and Disadvantages:

The advantages of DSSC are already discussed, at this stage we need to see what are the major disadvantages whose improvement by extensive research can make DSSC the best device for future energy harnessing

DISADVANTAGES:

The disadvantages are:

- These cells have low light to electricity conversion efficiency
- The major disadvantage to the DSSC design is the use of the liquid electrolyte, which has temperature stability problems. At low temperatures the electrolyte can freeze, ending power production and potentially leading to physical damage. Higher temperatures cause the liquid to expand, making sealing the panels a serious problem.
- Another major drawback is the electrolyte solution, which contains volatile organic solvents and must be carefully sealed. This, along with the fact that the solvents permeate plastics, has precluded large-scale outdoor application and integration into flexible structure.⁶⁸
- The electrolyte is: a) extremely corrosive, resulting in a lack of durability; b) densely coloured, preventing the efficient passage of light; and c) limits the device photovoltage to 0.7 volts⁸¹.
- The cathode is covered with platinum, a material that is expensive, non-transparent and rare⁸¹.

DSSCs are currently the most efficient third-generation⁶⁹ solar technology available. This makes DSSCs attractive as a replacement for existing technologies in small scale applications, where the mechanical robustness and light weight of the glass-less collector is a major advantage. Small increases in the DSSC conversion efficiency might make them suitable for large scale deployments as well.

Replacing the liquid electrolyte with a solid has been a major ongoing field of research. Recent experiments using solidified melted salts have shown some promise, but currently suffer from higher degradation during continued operation, and are not flexible.⁷⁰ Improvement studies in morphological and electrical characteristics of photoanode (the most important component of the DSSC), new sensitizers, hybrid electrodes, new electrolytes, and solid-state DSSCs for improving the efficiency of low cost solar cells are being pursued.

2.2.6. Fabrication of DSSC:

The main component of the DSSC is the photoanode, below is given a brief description of assembling DSSC emphasizing the fabrication of photoanode using titania nanoparticles which is the subject of research of the present work.

2.2.6.1. SYNTHESIS OF TITANIA NANOPARTICLES:

The oxide semiconductor most used in DSSC is TiO₂ in the anatase crystalline form. Other semiconducting oxides, like ZnO, SnO₂ and Nb₂O₅ have also been used in DSSC, but the cells exhibited lower performances in comparison to cells prepared with TiO₂. The TiO₂ is a wide bandgap semiconductor, $E_{bg} \sim 3.2$ eV. It is a non-toxic and inert compound, an inexpensive and readily available material.⁷¹ following are some of the common methods used for the synthesis of titania nanoparticles for DSSC applications:

(i) Sol-Gel/Hydrothermal Process:

M. Grätzel and co-workers⁶⁴ introduced a preparation method of TiO₂ nanopowder consisting of sol-gel synthesis and hydrothermal treatment. In a typical sol-gel/hydrothermal experiment, titanium isopropoxide is added drop-wise at room temperature to 0.1 M nitric acid solution under vigorous stirring. A white precipitate formed instantaneously. After that, the slurry is heated to 80°C and stirred vigorously for 8 h. To achieve peptization (i.e., destruction of the agglomerates and re-dispersion into primary nanocrystallites), the solution upon filtration to remove non-peptized agglomerates was diluted with water to adjust the final solids concentration to ~5 wt%. The final step of the process involved hydrothermal treatment in an autoclave for 12 h in the temperature range of ~220°C to enhance the crystallinity of the product.

(ii) Flame Synthesis⁷²:

Flame synthesis is used by Degussa to produce the commercially available nanotitania powder P25, which has been extensively investigated as candidate material for DSSC. This method typically involves the introduction of precursor TiCl₄ vapor into the reactor at a constant rate. Vapors decompose quickly, resulting in nanoparticle nucleation. TiO₂ nanoparticles were made at a furnace temperature of 1,473 K and a reaction residence time of only 2 s.

Other methods like aqueous synthesis, DC magnetron sputtering, template based sol gel method, anodization and metal organic chemical vapour deposition (MOCVD) are also used for synthesis of nanostructured materials for DSSC application.

2.2.6.2. FILM PREPARATION:

Preparation of the photoanode involves deposition of the TiO₂ nanoparticles on fluorine-doped tin oxide (FTO) glass, sintering/annealing, post-treatment, and sensitization. Nanoparticle deposition most commonly involves preparation of a paste and application by doctor-blade or screen printing. Alternatively, the nanoparticles may be dispersed in a liquid medium and deposited by spin or linear coating.

2.2.6.3. PROCESSING OF TiO₂ FILMS:

The temperature profile used in the sintering process has a great impact on the quality of the film. The maximum temperature should not exceed 550°C, because the phase transition from anatase to rutile starts in this temperature region, along with grain coarsening resulting in loss of nanostructure. The heating rate should be very slow. In the temperature interval 200°C < T < 350°C, organic materials such as dispersants and organic solvents used during the TiO₂ film deposition stage decompose. The decomposition process induces mechanical stress into the TiO₂ layer. If the heating is done too fast, the adhesion to the FTO substrate is not firm. Consequently, cracks form within the layer and the film becomes brittle. The cooling rate of the sintered TiO₂ electrode also needs to be slow in order to minimize the stress within the TiO₂ layer⁷².

2.2.6.4. ASSEMBLING OF DSSC:

After making sintered titania films over TCO coated glass, a monolayer of sensitizer dye is deposited on the surface of the semiconductor material by dip coating. Counter electrode is usually made of a very thin layer of an inert metal like Pt on TCO coated glass. Using a spacer in between the two electrodes are sealed. Then the electrolyte is injected into the sealed assembly to complete the cell configuration.

2.2.7. The Most Efficient DSSC to Date:

The most efficient DSSC that has been reported by M. Gratzel's group⁶⁴ consisted of a porous anatase TiO₂ film, deposited onto a transparent electrode, sensitized by the dye

RuII(2,2'-bipyridyl-4,4'-dicarboxylate)₂(NCS)₂ (also called N3 dye), an acetonitrile electrolyte with the redox couple I⁻/I₃⁻ and a Pt counter-electrode. The photocurrent measured at ca. 100 mW cm⁻² of simulated solar intensity (AM 1.5) was 20 mA cm⁻², the open circuit voltage, V_{OC}, was ~ 0.7 V, and the overall efficiency of the cell for light to electrical conversion was $\eta_{\text{global}} \sim 10\%$. The cell performance was still better under diffuse daylight, $\eta_{\text{global}} \sim 12\%$, revealing that the DSSC is less sensitive to light intensity variations than conventional photovoltaic devices, which is an important advantage for application in consumer electronic devices.¹⁰

2.2.8. Recent Developments in the Field of DSSC:

Jianguo Yu et al.⁷³ have fabricated Dye-sensitized solar cells using hollow anatase TiO₂ spheres synthesized by a chemically induced self-transformation (CIST) strategy using urea as a base catalyst, whose walls are composed of anatase nanocrystals and exhibit hierarchical porosity. The best performance is obtained at calcinations temperature of 600°C and the efficiency is found to be 4.82% as compared to 4.35% for Degussa TiO₂ nanoparticles. The enhanced performance of HA-TiO₂ cells is due to their high surface area and hierarchically nanoporous structures when compared with the nonporous TiO₂ nanoparticles.

E. Ohayon and A. Gedanken⁷⁴ have prepared highly crystalline metal oxide nanoparticles of TiO₂, WO₃, and V₂O₅ by reacting transition metal chloride with benzyl alcohol using ultrasonic irradiation under argon atmosphere in a non-aqueous solvent in just a few minutes. The temperature used is 363 K. The particles' size and shape measured from HRSEM reveal "quasi" zero-dimensional, spherical TiO₂ particles in the range of 3–7 nm. The mechanism of the reactions leading to these three metal oxide nanoparticles in a non-aqueous system is substantiated by Nuclear Magnetic Resonance (NMR), and Electron Spin Resonance (ESR).

K. Yuan et al⁷⁵ prepared ZnO nanoarrays by a simple chemical bath deposition method on the glass slide deposited with a spin-coated ZnO seed crystal layer. The characterization results show that the ZnO nanoarray is the hexagonal wurtzite structure and grow along the [0 0 1] axis. Furthermore, the energy-conversion property of the device was

investigated in such ZnO nanoarray constructed dye-sensitized solar cells (DSSCs), which has potential applications in the new-concept photovoltaic devices.

Modifying the TiO₂ electrode-sensitized dye interface, Calcium oxide or lithium fluoride, evaporated on the surfaces of thin film electrodes based on TiO₂ nanoparticles and nanotubes, can enlarge N719 dye adsorption content of the photo-electrode layer, and thus improve the electron injection flux. **R. H. Lee and Y. W. Huang**⁷⁶ have investigated this aspect and they find that the presence of an energy barrier layer would prevent electrons already injected into the electron transport layer from returning to the dye layer. This thermal deposition technique effectively improves the injection efficiency of electrons, and in turn, also promotes the solar energy conversion efficiency of the DSSCs.

As sealing of a DSSC is a major problem, to reduce the area to be sealed, **Z. Tachan et al.**⁷⁷ have fabricated a DSSC inside a glass tube for the making of a dye-sensitized solar tube (DSST). FTO is deposited inside a glass tube by spray pyrolysis. A mesoporous TiO₂ film is then deposited over the FTO. After sintering sensitized with a Ru-dye (N3) and immersed into it a redox electrolyte while a Pt-coated rod closed the electrical circuit. Another huge advantage of the tube design is the possibility to incorporate a current collector without blocking direct sunlight from entering the cell. The cylindrical shape of the DSST can be used to collect diffuse light more effectively. The light to electric power conversion efficiency of 2.8% has been achieved.

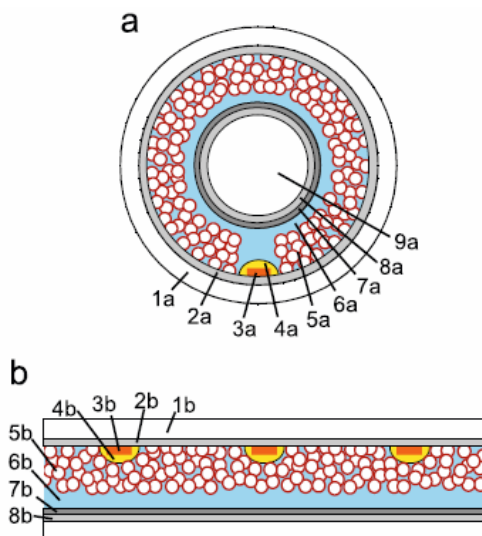


Fig. 2.3(a) Schematic cross-section of a dye-sensitized solar tube (DSST) showing the glass tube (1a), the FTO layer (2a), a highly conducting current collector attached to the FTO on the bottom side inside the DSST (3a) and a polymer layer, which is protecting the current collector (4a). The mesoporous dye-sensitized TiO₂ film (5a) deposited on to the FTO is immersed into the redox electrolyte (6a). The circuit is closed by a counter electrode consisting of a sputtered Pt layer (7a) on top of a sprayed FTO film (8a), deposited on to a quartz rod (9a).

A 3D DNA-like structured dye-sensitized solar cell (DSSC) (Fig 2.4) with all-Ti substrates is reported by **Y. Wang et al**⁷⁸ they have grown a self organized TiO₂

nanotubular arrays layer directly on the photoanode surface by electrochemical anodization. The DNA-like DSSC showed superiority of light utilization due to its symmetrical double-helix structure. It is anticipated that the novel DNA-like structured DSSCs have great application potential in larger modules using integrated circuit.

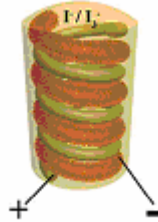


Figure 2.4. DNA like DSSC

Y. Wang et al.⁷⁹ have reported a two-step formation of a TiO₂ nanowire-covered nanotube bilayer film technique and its application in DNA-like dye-sensitized solar cells (Fig. 2.5). The bilayer film was prepared by the electrochemical anodization first and then the hydrothermal method. From the reflectivity spectrum and scanning electron microscopy it is observed that the nanowire layer on the top cannot only decrease the reflectivity of the film, but also play a role to modify the film cracks. Compared with the dye-sensitized solar cells based on a single layer electrode, the cell with the bilayer film showed higher photovoltaic parameters and a lower dark current, which is due to its higher light harvesting efficiency and lower charge recombination between the electrolyte and the substrates.

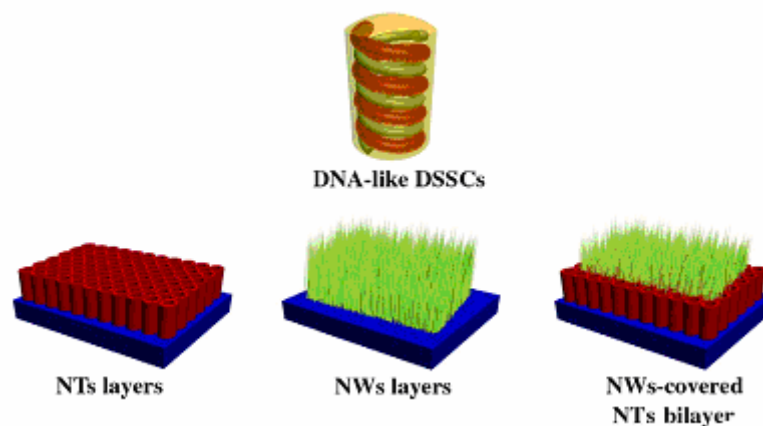


Figure: 2.5: Nanowire covered nanotube bilayer and its use in DSSC

A 3-dimensional dye-sensitized solar cell (3D-DSSCs) and module (Fig.2.6) simulating the fractal structure of the pine tree for capturing sunlight is reported by **Y. Liu**

et al.⁸⁰ Compared to traditional flat solar cells, this type of solar cell exhibits superiority of absorbing sunlight from all directions. The fabricated 3D-DSSC and module have achieved 3.36% and 3.19% efficiencies, respectively.

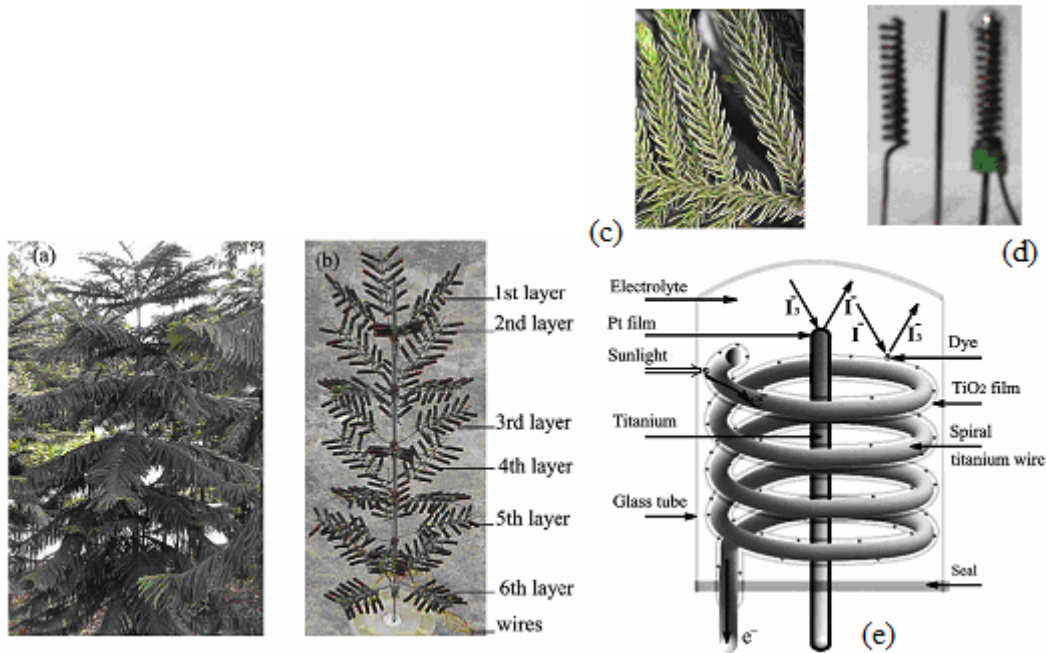


Fig. 2.6. Picture and schematic of 3D-DSSC module. (a) Picture of pine tree. (b)

Picture of 3D-DSSC modules simulating the tree-like structure. (c) Picture of the needle leaves growing around the stem in screw pattern on the shoot. (d) Picture of spiral photo-electrode, counter electrode and 3D-DSSC, respectively (electrolyte is not injected to obtain a clear picture). (e) Schematic structure and principles of the 3D-DSSC.

B. Marsan, L. Breau et al.⁸¹ have developed a new transparent and non-corrosive liquid or gel electrolyte which can increase the photovoltage, thus improving the cell's output and stability. They have also found that Cobalt sulphide can replace the Platinum metal as a cheap, stable and efficient cathode in DSSC.

Above is quoted only a few examples from the extensive work being done all over the world in this field. There is great potential in DSSC to be used as primary green energy source of the near future. The present work is a small contribution of effort in this field.

2.2 OBJECTIVES:

The long run objective of this project is to produce low cost and highly efficient dye sensitized solar cells to assist with the mounting electricity needs of our country. This masters research work is ought to be a first step towards the achievement of our main goal.

For MS thesis the main objectives are:

- To prepare and optimize the semiconductor oxide (titanium dioxide) nanoparticles for use in the making of photoanode of the DSSC. Sol gel refluxing method is opted for this purpose.
- To grow one dimensional nanostructures of above material over TCO coated glass to offer maximum surface area for maximum adsorption of sensitizer and in short, for higher efficiency.
- Making of pastes for deposition of nanoparticles over the TCO coated glass to produce a film of sintered nanoparticles with high surface area.
- Deposition of films using above pastes and their characterization.

These are the main goals to be experimented. Besides other experiments may also be tried like making of a prototype DSSC using available resources.

CHAPTER 3

MATERIALS AND METHODS

This piece of research consists of a passionate effort to move towards the fabrication of low cost and highly efficient dye sensitized solar cells. Following are the main aspects over which experimentation was done.

- Synthesis of a precursor wide band gap semiconductor
- Use of above precursor to make nanostructured thin films on TCO coated glass.

Experimentation:

- All chemicals and materials were of analytical grade
- The chemicals were used as obtained without further purification.

3.1. SYNTHESIS OF TITANIA NANOPARTICLES

METHOD 1:

12g (0.2 moles) of glacial acetic acid (Sigma-Aldrich) was added to 56.852g (0.2 moles) of Ti (IV) tetraisopropoxide (TTIP) (97% Aldrich) under stirring at room temperature. After 15 minutes 290ml of distilled water was added as quickly as possible with vigorous stirring. An instant white precipitate resulted. The mixture was stirred for 1 hour to ensure complete hydrolysis. Then 4 ml of conc. HNO_3 was added and the mixture was heated from room temperature to 80°C within 40 minutes and peptized for 75 minutes. Distilled water was added to make the volume 370 ml.⁸²

The above sol was then subjected to refluxing at 100°C for different durations given in table 3.1.

The resulting gel was exposed to ultrasonic radiations (Cole-Parmer-08895-46 ultrasonic bath) for 20 minutes. The pH was kept in the range of 1 -2. Water was removed from the gel using rotary evaporator and ethanol was added to make 40 wt % TiO_2 gel.

Sr. No.	Samples	Refluxing time (hrs)
1.	Tit1	24
2.	Tit2	70
3.	Tit3	120

Table 3.1: Refluxing time for samples Tit 1, Tit 2, Tit 3.

Annealing: A part of the gel was dried at 60 ° C and afterwards annealed at 450°C for 40 minutes in Nabertherm GmbH N17/ HR- 400V Muffle furnace. The heating rate was kept 1.8 ° C per minute.

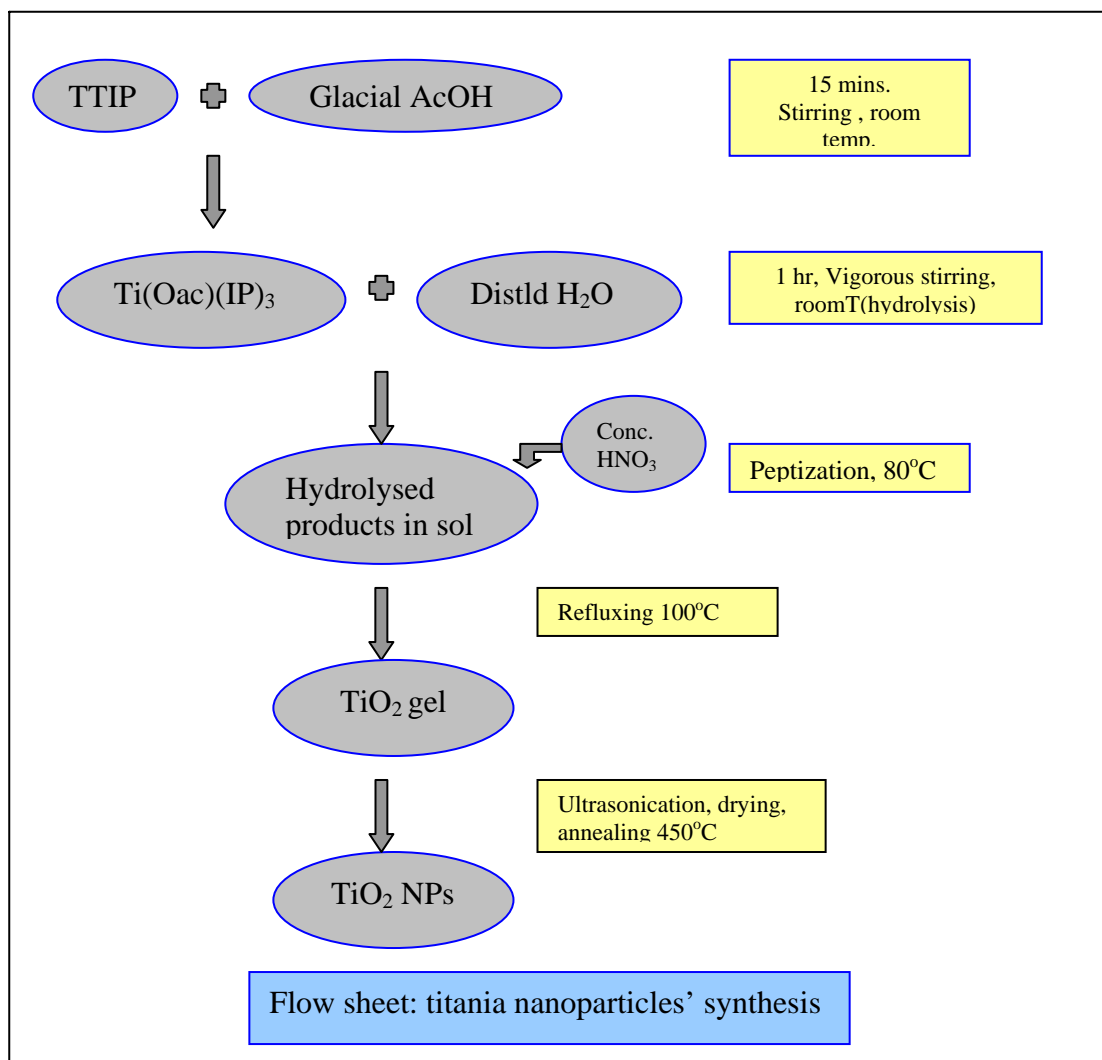


Figure 3.1: Flow sheet for titania nanoparticles synthesis (method 1)

METHOD 2:

5g (0.05 mole) acetyl acetone (Merck) was added to 14.213g (0.05mole) of TTIP (97% ,Aldrich) under stirring at room temperature⁸⁴. The mixture was stirred at room temperature for about half an hour. 75 ml of distilled water was added at once with vigorous stirring for one hour. Then 1 ml of conc. HNO₃ was added to obtain clear yellow solution. It was then heated to 60°C and kept at this temperature for two hours. After two hours distilled water was added to make the volume 100 ml. The clear yellow solution was then subjected to refluxing.

Sr. No.	Samples	Refluxing time (hours)
1.	Ta1	24
2.	Ta2	65

Table 3.2: Refluxing time for samples Ta 1, Ta 2

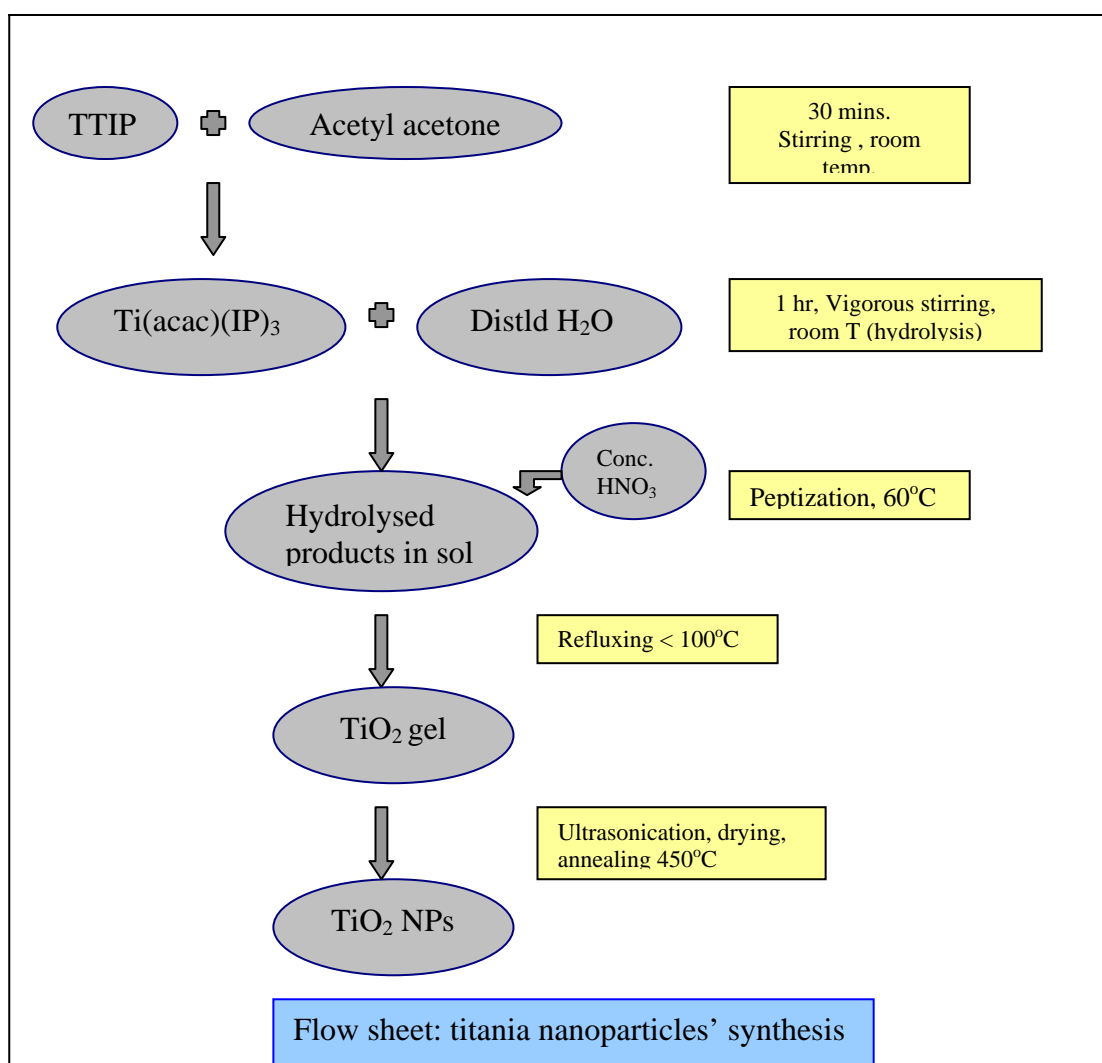


Figure 3.2: Flow sheet for titania nanoparticles synthesis (method 2)

After refluxing a whitish gel was obtained. The gel was dried at about 60°C in an oven and grinded.

Annealing was performed at 450°C in a muffle furnace in air for 40 minutes.

ANALYSIS:

3.1.1. Preliminary Analysis:

Colour, odour and Solubility:

Colour and odour were observed. After drying of above gels the solubility of the powder was tested in different solvents like water, ethanol, 2-propanol, acetyl acetone and acids.

3.1.2. XRD Analysis:

The gel was dried at 60°C and grinded to make fine powder which was exposed to X-rays in Stoe D-64295 Darmstadt X ray Diffractometer for inspecting the material, its phase and the average crystallite size.

The powder was annealed at 450°C for 40 min and analysed for phase and crystallite size.

3.1.3. Scanning Electron Microscopy (SEM):

Powder product was mounted on a copper stub and after gold sputtering was observed in JEOL JSM-6460 SEM.

Dispersions in different dispersants like water, ethanol. Acetylacetone and sodium hexametaphosphate were made for observing the morphology of the particles.

For the compositional analysis energy dispersive X-ray spectroscopy was used in JEOL JSM-6460 EDS.

3.2. PASTE FOR THIN FILM OF TITANIA NANOPARTICLES:

0.3 g of TiO₂ powder, 0.3 g polyethylene glycol (Merck), 6 ml ethanol absolute (Merck), 0.1 ml acetyl acetone (Merck) and 1 drop of glacial acetic acid⁸³ were mixed in a bottle, glass balls were added into the bottle and after covering with an air tight cap, the bottle was put on milling on hand made ball mill for 5 days. Only Tit 1, Tit 2 and Tit 3 were used to make pastes.

3.3. MAKING THIN FILMS BY DOCTOR BLADING:

The above pastes were used to make few micron thick film over plain glass and TCO coated glass by following procedure: 0.2mm boundaries were made on 2.5 cm × 2.5 cm glass slides and 3 × 2cm FTO coated glass using a scotch tape, a small amount of the paste was poured on one side of the substrate and then it was spreaded by a razor to make a uniform film. The films were dried in air at room temperature.

Annealing of the films: The above films were annealed in a muffle furnace at 450°C for 40 minutes. The heating rate was about 1.8° C per minute.

ANALYSIS:

3.3.1. TGA/DSC Analysis:

The dried pastes were subjected to thermal gravimetric analysis and differential scanning calorimetry in Perkin Elmer TGA/DTA analyser to see for the removal temperature of the organic additives and the phase change if any occurs.

3.3.2. Optical Microscopy:

The films were observed under the transmission optical microscope (MBL 2100 Kruss Optronic, Germany) before and after annealing and images were taken.

3.3.3. SEM and EDS Analysis:

The films were observed under SEM and EDS was done to study morphology and the composition of the films before and after annealing.

3.3.4. Surface Area Measurement:

The surface area was measured by BET method of the dried and annealed thin films for comparison and optimization of the work.

3.4. MONOLAYER OF N3 DYE OVER TITANIA FILM:

The sintered films were dipped in 10⁻⁴ M solution of N3 dye for about 24 hours and after rinsing were dried in air. After this a photoanode was ready for a dye sensitized solar cell (DSSC).

3.5. MAKING OF COUNTER ELECTRODE FOR DSSC:

FTO coated glass pieces of 2 × 3 cm were coated with gold using automatic JEOL JFC-1500 Ion Sputtering Device after cleaning with ethanol. The thickness of the film was set to be 400 Angstroms.

3.6. ASSEMBLING OF DSSC:

A dye sensitized photovoltaic cell was assembled. Silver paste was applied on one edge of each electrode. One drop of KI/ Iodine electrolyte in ethylene glycol was put on the dye sensitized titania film of the photoanode after using a spacer Surlyn of around 40 micron thickness. The counter electrode was then put over the photoanode and clipped using two binding clips.

3.7. TESTING OF THE CELL:

Current producing tendency of DSSC was checked a light of intensity 100 mW/cm², using Keithley 2410 source meter.

3.8. SPUTTER COATED ALUMINUM FILM OVER TCO COATED GLASS:

A DC magnetron sputter system was used for the deposition of Aluminum over cleaned TCO coated glass. 99.99% pure Al target with 3" diameter was used. Power was 100 W. The base and working pressures were 6.05×10^{-6} mbar and 3.30×10^{-3} mbar. Ar was used as sputtering gas at a flow rate of 7 sccm. About 10 μm thick layer was deposited.

ANALYSIS:

3.8.1. Physical Appearance:

The physical appearance was observed.

3.8.2. XRD Analysis:

XRD analysis was performed in Stoe D-64295 Darmstadt X ray Diffractometer for structure and phase analysis.

3.8.3. SEM and EDS:

A piece of Al coated glass was mounted on a stub and was observed under SEM to see the surface morphology. For thickness measurement a piece was mounted vertically on the stub and the thickness was then measured in JEOL JSM-6460 SEM.