

# **Fabrication of Carbon Nanomaterials based Counter Electrode for Dye Sensitized Solar Cells**



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Session 2015-17**

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**U.S Pakistan Center for Advanced Studies in Energy  
National University of Sciences and Technology  
H-12, Islamabad, Pakistan  
July 2018**

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**A Thesis Submitted to *U.S Pakistan Center for Advanced Studies in Energy* in partial fulfillment of requirement for degree of Master of Science in**

**ENERGY SYSTEM ENGINEERING**

**U.S Pakistan Center for Advanced Studies in Energy**  
**National University of Sciences and Technology**  
**H-12, Islamabad, Pakistan**  
**July 2018**

## **THESIS ACCEPTANCE CERTIFICATE**

Certified that final copy of MS thesis written by Muhammad Awais Mahboob, (Registration No. 00000117685), of USPCAS-E, has been vetted by undersigned found in all respect NUST Statues/Regulations, is free of plagiarism, error, and mistakes and is accepted as partial fulfillment for award MS degree. It is further certified that necessary amendments as pointed out by GEC members of the scholar have also been incorporated in the said thesis.

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# Certificate

This is to certify that work in this thesis has been carried out by Muhammad Awais Mahboob and Completed under my supervision in U.S Pakistan Center for Advanced Studies in Energy (USPCAS-E), National University of Sciences and Technology, H-12 sector, Islamabad.

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# Dedication

To,

My father who gave me the greatest gift “He trusted me”

My mother who was there to support when every else deserted me.

To my family who took my troubles as their own.

To my teachers who instilled the love of learning in me.

To my friends who are the most valuable asset I have. Who supported me and helped me.

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# Abstract

The main idea behind this research is the fabrication of low cost and efficient solar cells, which will make this technology economically feasible. The task of this research is to fabricate carbon nanomaterial based counter electrode for dye sensitized solar cells (DSSCs). DSSCs are 3<sup>rd</sup> generation solar cells which are traditionally fabricated employing platinum based counter electrode. Since platinum is expensive and being a rare earth metal so there is need to explore highly conductive and abundant material which could replace it. Recently metal oxides like NiO and carbon nanotubes (CNTs) have been proposed as efficient counter electrodes. In this work, a composite of NiO-CNTs is prepared as it shows potential to perform better as compared to NiO and CNTs alone. Multiple walled CNTs are dispersed in two polymers: PEDOT: PSS and polyvinyl propodilene (PVP) in 1:20 ratio. Counter electrodes of DSSC, are fabricated from NiO, CNTs and NiO-CNTs composite to compare the electrical properties of the counter electrodes. Results obtained from Hall Effect confirm the higher conductivity of NiO-CNTs composite. Transmittance of these three counter electrodes is also measured, which shows that these electrodes can transmit more than 70% of the light so these electrodes are suitable for transparent solar cells. Complete dye sensitized solar cells based on these counter electrodes are also assembled to check the efficiency of the solar cells.

## Table of Contents

1.1	Renewable Energy .....	15
1.1.2	Worldwide renewable energy.....	16
1.1.3	Renewable energy in Pakistan.....	17
1.2	Fundamental working of Photovoltaic (PV).....	20
1.3	Generations of solar cells.....	24
1.3.1	First Generations solar cells .....	25
1.3.2	Second Generations solar cells.....	25
1.3.3	Third Generations solar cells.....	25
	Chapter summary .....	31
	Reference .....	32
2.1	Dye sensitized solar cells .....	34
2.2	Structure of Dye sensitized solar cell.....	36
2.2.1	Photo Anode.....	37
2.2.1.1	TiO <sub>2</sub> Photo anode.....	37
2.2.1.2	ZnO photo anode .....	37
2.2.2	Dye: .....	38
2.2.3	Electrolyte .....	39
2.2.4	Counter Electrode.....	40
2.2.4.1	Platinum as a counter electrode .....	40
2.2.4.2	PEDOT: PSS counter electrode .....	40
2.2.4.3	Carbon nano materials based counter electrode .....	41
2.2.4.4	Metal oxide as counter electrode .....	42
2.2.3	Working principle of dye sensitized solar cell .....	43
	Chapter summary .....	46
3.1	Deposition technique for counter electrode.....	51
3.1.1	Electrospinning technique .....	51



3.1.1.1 Working Principle of electrospinning.....	53
3.1.1.2 Stepwise procedure of Electrospinning .....	55
3.1.2 Spin coating.....	56
3.1.3 Chemical Vapor deposition (CVD) Technique.....	58
3.2 Characterization techniques .....	60
3.2.1 Scanning electron microscope (SEM).....	60
3.2.2 Energy dispersive spectroscopy (EDS).....	62
3.2.3 X-ray Diffraction (XRD).....	62
3.2.4 Hall Effect .....	64
3.2.5 Cyclic Voltammetry (CV).....	67
3.3 Assembling of complete DSSC .....	69
3.3.1 Characterization of DSSC .....	70
Chapter summary .....	74
Reference:.....	75
4.1 Materials .....	77
4.2 Growth of Nanomaterials.....	77
4.2.1 Growth of carbon nanotubes .....	77
4.2.2 Growth and preparation of NiO and NiO-CNTs composite by co-precipitation method.....	79
4.3 Solution preparation for electrode deposition .....	81
4.4 Fabrication of counter electrode by spin coating .....	82
4.5 Assembling of complete Dye sensitized solar cell.....	82
Chapter summary .....	84
Reference:.....	85
5.1 Morphological, compositional and structural analysis .....	87
5.1.1 SEM, EDS and XRD analysis of CNTs .....	87
5.1.2 SEM, EDS and XRD analysis of NiO.....	90

5.1.3 SEM, EDS and XRD analysis of NiO-CNTs:.....	94
5.1.4 Morphology of deposited films:.....	98
5.2 UV-Vis spectroscopy analysis:.....	100
5.3 Electrochemical analysis by cyclic voltammetry.....	101
5.4 Electrical properties of deposited film by Hall Effect.....	105
5.5 Efficiency comparison of DSSCs.....	105
Chapter summary.....	108
Reference.....	109
6.1 Conclusion:.....	111
6.2 proposed future works:.....	111
Publications:.....	113

# List of Figures

Figure 1: Global carbon emission from fossil fuels 1900-2014.....	13
Figure 2 Total U.S Greenhouse Gas emissions.....	14
Figure 3: Worldwide energy consumption of year 2015 .....	15
Figure 4: PV installed worldwide .....	17
Figure 5: Power sector in Pakistan.....	18
Figure 6: The estimated renewable energy potential .....	19
Figure 7: Advantages of renewable energy in Pakistan.....	20
Figure 8: Structure of a typical solar cell.....	21
Figure 9: Current-voltage curve of a solar cell .....	23
Figure 10: Multi junction solar cells .....	26
Figure 11: Working principle of Q dot solar cell.....	27
Figure 12: Working principle of Perovskite solar cells .....	28
Figure 13: Working principle of DSSCs.....	29
Figure 14: Number of Research papers in each year .....	35
Figure 15: Structure of DSSC .....	36
Figure 16: Working diagram of Dye sensitized solar cell .....	43
Figure 17: FLUIDNATEK LE 10 at USPCASE NUST .....	53
Figure 18: Control panel on electospinner.....	54
Figure 19: Flow rate control .....	55
Figure 20: Spin coater in energy materials lab at USPCASE NUST.....	56
Figure 21: structure of spin coater .....	57
Figure 22: vacuum pump attached with spin coater .....	57
Figure 23: Schematics representation of steps of CVD process .....	59
Figure 24: CVD schematic diagram for CNTs activation .....	59
Figure 25: internal structure of scanning electron microscope (SEM) .....	61
Figure 26: working principle of SEM.....	62
Figure 27: Bragg's law as working principle of XRD.....	63
Figure 28: XRD machine (D-8 Advance) available at USPCASE .....	64
Figure 29: hall Effect measurement equipment at USPCASE NUST .....	65
Figure 30: Sample-mounting board .....	66
Figure 31: Sample kit with 0.55 Tesla magnet supplied standard with the system ...	66

Figure 32: Complete assembly of DSSC using microfluidic technique .....	70
Figure 33: Solar simulator in advance energy materials lab at USPCASE NUST ....	72
Figure 34: output curve of IV measurement of solar cell at AM 1.5 .....	73
Figure 35: CVD setup for preparation of CNTs .....	78
Figure 36: Flow diagram of preparation of functionalized CNTs .....	78
Figure 37: Flow diagram of preparation of NiO nanocomposite.....	80
Figure 38: Process flow diagram for preparation of NiO-CNTs .....	81
Figure 39: CNTs at 5um resolution .....	87
Figure 40: Mapping of CNTs on SEM image at high resolution.....	88
Figure 41: EDS results of the CNTs .....	89
Figure 42: XRD analysis of CNTs.....	90
Figure 43: Mapping of NiO on SEM image at 1um resolution .....	91
Figure 44: EDS analysis of NiO .....	92
Figure 45: XRD analysis of NiO .....	93
Figure 46: SEM image of NiO-CNTs at 5 um.....	94
Figure 47: Mapping of NiO-CNTs on SEM image at 1um resolution .....	95
Figure 48: Line EDS analysis of NiO-CNTs .....	96
Figure 49: XRD analysis of NiO-CNTs.....	97
Figure 50: SEM of NiO-CNTs at 5um.....	98
Figure 51: SEM image of NiO-CNTs deposited on PET at 500nm .....	99
Figure 52:EDS analysis of NiO-CNTs .....	99
Figure 53: Transparency of NiO-CNTs, CNTs and NiO based counter electrode ..	101
Figure 54: CV results of NiO.....	102
Figure 55: CV result of CNTs.....	102
Figure 56: CV result of NiO-CNTs.....	103
Figure 57: Cathodic and anodic reaction on CV curve.....	104
Figure 58: Comparison of IV measurement of NiO, CNTs and NiO-CNTs based DSSC.....	106

# List of Tables

Table 1: Comparison between semiconductor solar cell and Dye sensitized solar cell .....	35
Table 2: Solution composition .....	82
Table 3: Percentage of elements in CNTs.....	89
Table 4: percentage composition of NiO .....	92
Table 5: EDS results of NiO-CNTs .....	96
Table 6: Compositional analysis of NiO-CNTs coated film.....	100
Table 7: comparison of properties on basis of Hall Effect .....	105
Table 8: Comparison of DSSC based on counter electrode from NiO, CNTs and NiO-CNTs.....	107

# Chapter 1: Introduction

Energy is the most important need of human life today. Energy is being used for industrialization, transportation, domestic and household utilization and to meet the standard lifestyle of the modern era. Energy is although improving our lifestyle and creating ease for us but on the other hand, it is also creating hazards for the environment. Since the beginning of human history, Energy is being produced by the burning of fossil fuel. Fossil fuels produce greenhouse gasses which are very dangerous for all living things on the planet. The increase in the amount of CO<sub>2</sub> is the result of the burning of fossil fuel to get energy from fossil fuel in a suitable form. Increase in CO<sub>2</sub> concentration would lead to air pollution, which would cause health problems for all living things and on plants. Gases produced in fossil fuel combustion like Sulfur dioxide and nitrogen oxide can cause acidic rains. Ozone layer depletion is also a result of pollution caused by energy resources. Hence the main problems of the day are depletion of fossil fuel and climate change. crude oil emits 3.15 kg Carbon per barrel of oil equivalent (Boe), natural gas emits 2.28 kg, coal emits 4 kg of carbon and for gas to liquid 2.63 kg of carbon is being emitted[1].

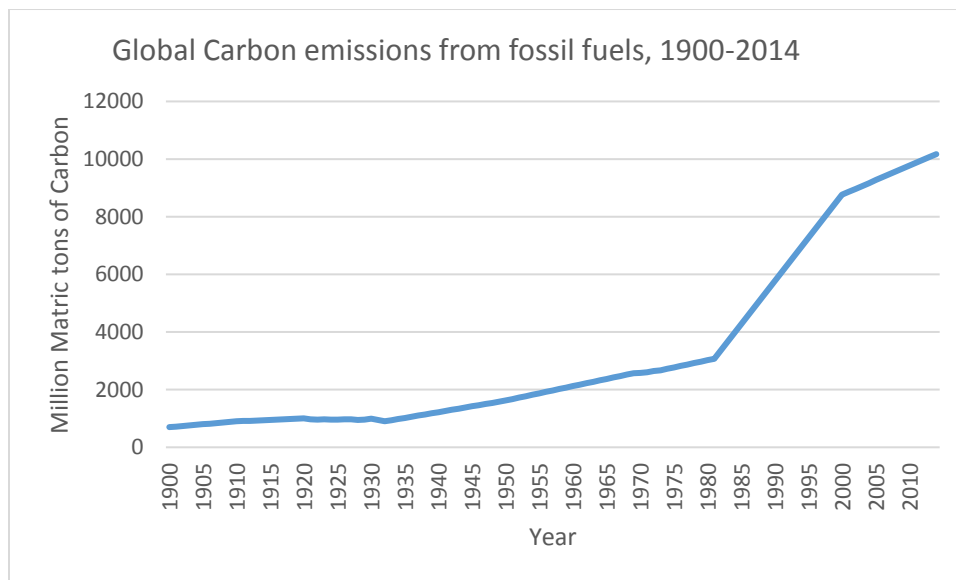


Figure 1: Global carbon emission from fossil fuels 1900-2014

It is clear from Figure 1, which is based on data by Environment protection agency (EPA), GHGs increased until 2005. Since 2006 there was a boom of renewable energy and strict environmental

protection laws, GHGs were controlled and since then it is decreasing so there is a decrease in the rate of greenhouse gasses. Environmental temperature is increasing by 0.13 °C per decade due to global warming. Environment temperature is expected to reach a minimum of 2 °C above pre-industrial. Global warming is not only increasing environmental temperature but also causing melting of ice due to which marine life is in high danger. The ozone layer is also depleting due to greenhouse gas effects. There is need of environment-friendly and sustainable energy resource which could sustain for centuries. There are many sources of nature which human being are using since the beginning to meet their energy demand. Sun, wind, water, and coal are types of resources which humans are using since a long ago.

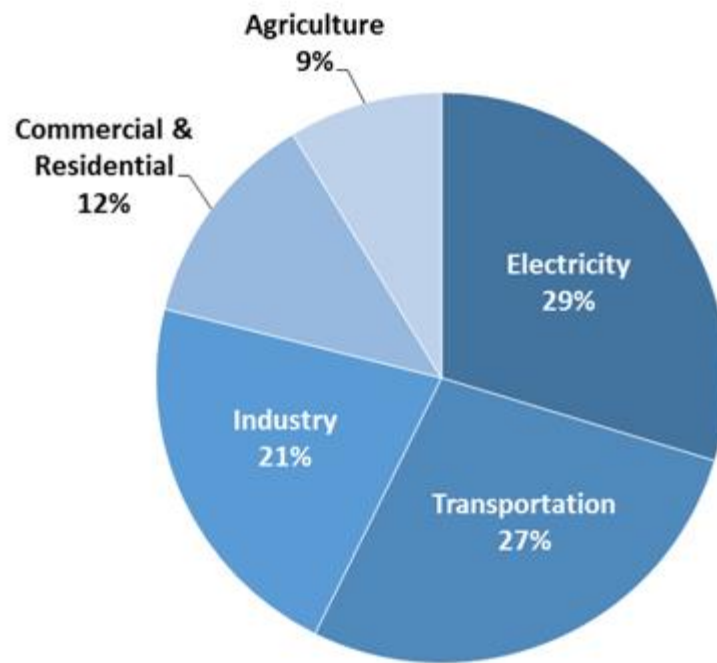


Figure 2 Total U.S Greenhouse Gas emissions [2]

There is also the issue of fossil fuels depletion with the passage of time. Fossil fuels cannot be eliminated in short time but it will take decades to shift our dependency from fossil fuel to clean and widely available energy resources. According to The International Energy Agency (IEA), oil demand will reduce from 35% to 32% by 2030. Fossil fuels production has reached its peak point and this production will be reduced in future. According to the Klass, model oil will deplete in 34 years, coal in 106 years and gas in 36 years. Coal resources of the world have been downgraded from 1980 to 2005 by an overall 50%. [3].

## 1.1 Renewable Energy

Renewable energy is becoming burning issue worldwide due to fossil fuels depletion and global warming. The demand for renewable and clean energy is increasing day by day. Biomass, solar energy, wind, tidal and geothermal are types of renewable energy.

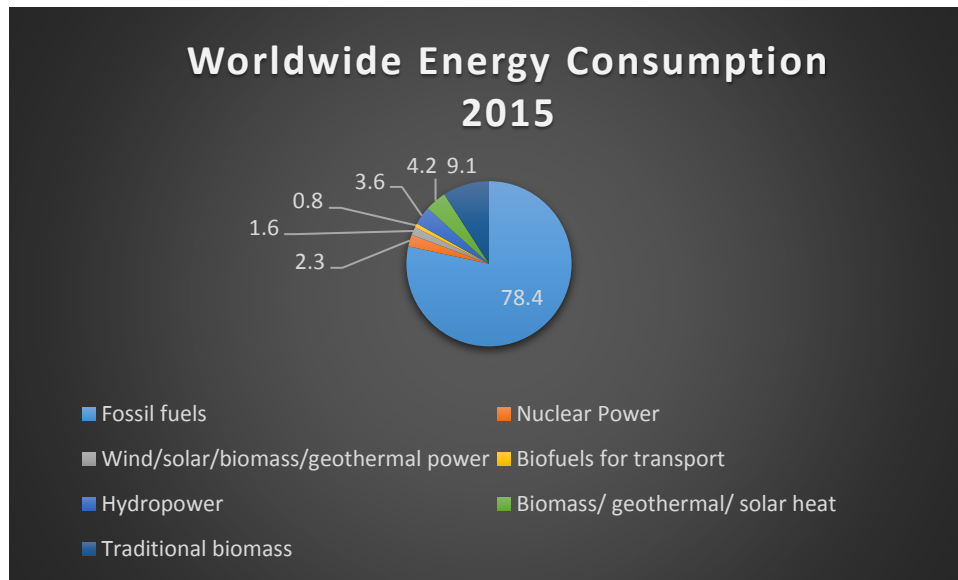


Figure 3: Worldwide energy consumption of year 2015 [8]

The efficiency of renewable energy was very less at the start but due to extensive research on renewable energy resources, these got developed with the passage of time. Cost of renewable energy was very high due to which it could not these were not being adopted in the 20<sup>th</sup> century, for example, wind energy cost was about 30cents/kWh in 1980 and then dropped to 5cents/kWh due to which wind energy became feasible [4]. Similar results are for solar energy. Solar energy price was very high around \$100/kWh but this has reduced to few dollars per kWh. Electricity cost produced from solar energy was around 30-40cents/kWh in 1970 which now has reduced to 3-4 cents/kWh. According to the anticipation of International Energy Agency by 2050 solar energy will occupy 25% of the energy market and similar to wind energy as well. Similarly, geothermal energy is expected to reach 17.6 GW till 2020. Biomass is also a huge source of renewable energy. Biomass to gasoline technology created the potential for biomass to replace fossil fuels. Biodiesel is being produced from biomass which is going to replace conventional diesel. The graph below shows that fossil fuels are highest consuming in the field of energy while renewable is less



consuming yet but with the passage of time consumption of renewable resources are going to increase [5].

### **1.1.1 Solar Energy**

Solar energy is a very important type of renewable energy. Solar energy is obtained when sun light is being converted to different forms of energy depending upon the requirement. Light from sun consists of multiple wavelengths and depending on wavelength. Solar spectrum consists of Infrared region (700nm-1mm), visible region (380-780nm) and Ultraviolet region (UV) (100-400nm) of the electromagnetic radiation. These spectrums are very important to get maximum output from a solar cell. A solar cell is considered better which could utilize a maximum of the solar spectrum. Solar energy can be supposed to be the most abundant energy source as the sun will keep on shining for billions of years. According to International Energy Agency (IEA), solar energy can produce up to 885 million terawatt-hours (TWh) in a year that is 6200 times of the energy being consumed worldwide in 2008 and 4200 times the energy consumption expected in 2035. There are further three types of solar energy, Photovoltaic solar power, solar thermal energy and concentrated solar power. Solar energy is used to produce different forms of energy. The output of Solar photovoltaic (PV) is electrical energy while the output of solar thermal energy is steam which can further be used for heating or power generation. The output of concentrated solar power is electrical power and steam depending on the type of power plant. Among these, all types of solar energy, Solar PV is type on which major research is being focused due to which efficiency of PV is increasing with time and price of PV systems is decreasing day by day[6].

### **1.1.2 Worldwide renewable energy**

Renewable energy is gaining importance in the world with the passage of time. Cost of the renewable is reducing while technology is improving with the passage of time.

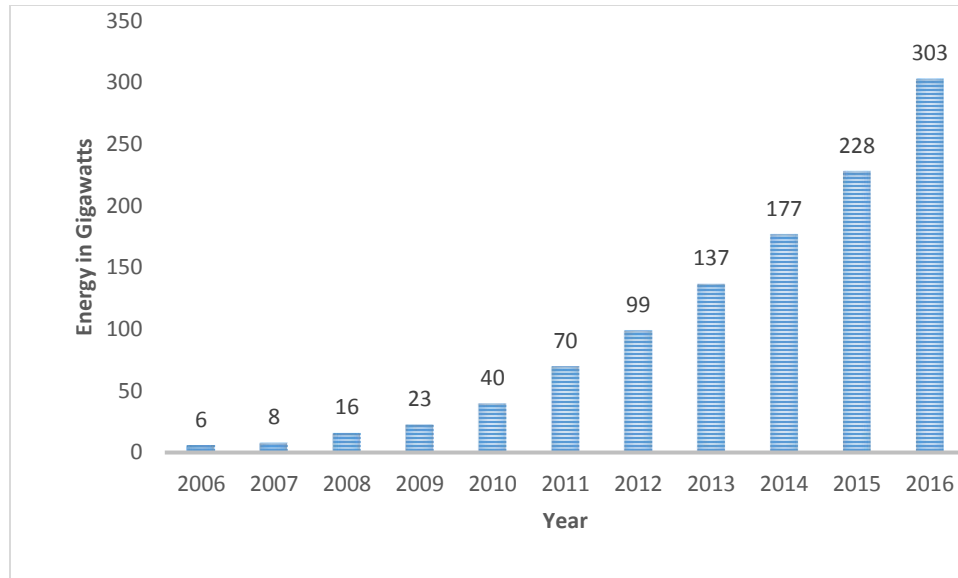


Figure 4: PV installed worldwide

The graph in Figure 4 shows that photovoltaic energy installation is increasing worldwide at a high rate. Increase in energy resources in the year 2015-2016 was even more than 30%. In China installation of PV increased by 34% and the USA increased PV capacity by 15%. Solar water heating capacity has reached to 450 GWs. Wind energy installed capacity has reached up to 480 GW. China invested around 40 billion US dollars on PV in the year 2015 alone. United nation framework for conventional climate change (UNFCCC) is an organization which works with clean energy resources. UNFCCC benefit the countries by giving financial assistance in the field of renewable energy[4][7].

### 1.1.3 Renewable energy in Pakistan

Pakistan also adopted renewable energy likewise other countries. Pakistan has installed power capacity of 17000MW while peak demand is around 22000MW [8]. Therefore, energy demand is increasing at a rate of 10% annually. Energy requirement would reach up to 45000 MW till 2030[9].

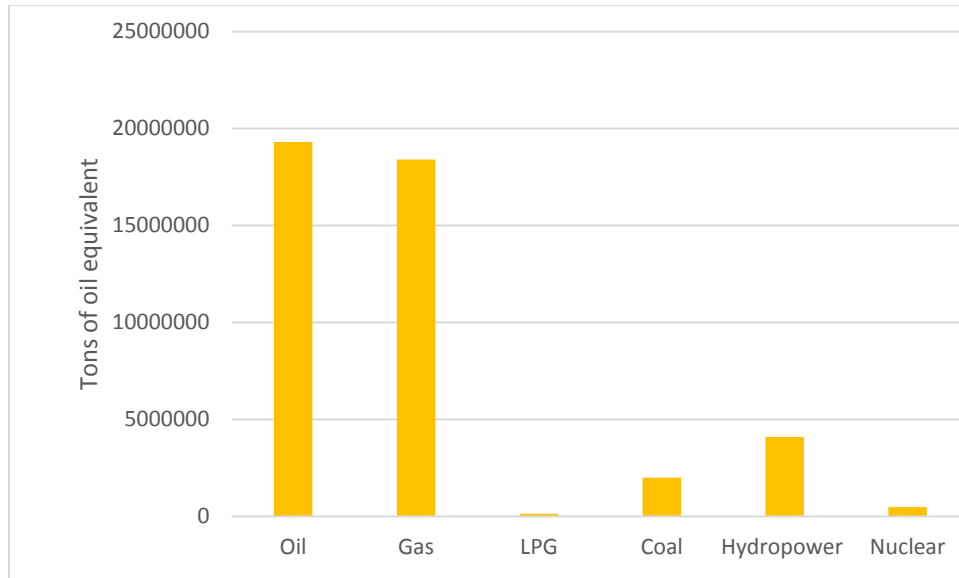


Figure 5: Power sector in Pakistan [8]

The Figure above shows the share of energy resources in power sector of Pakistan. It clearly shows that Pakistan is mostly dependent on oil and gas resources to meet its energy demand. The share of other energy resources especially renewables are negligible. Due to high consumption of oil and gas, Pakistan is facing the problem of pollution and a higher concentration of greenhouse gases in the environment[10][11].

Pakistan has a high potential for renewable energy as shown in Figure 6. Potential of photovoltaic solar energy is very high. Cost of photovoltaic solar panels was very high till 2010 but now it is reducing due to Government friendly policies towards renewable energy resources. Pakistan is located in a region where solar insolation is very high. Average sun hours per day is around 7 hours/day during summer which is very high value. Pakistan has set a target of getting 10,000MW of electricity through renewable energy till 2030 [12][13][14].

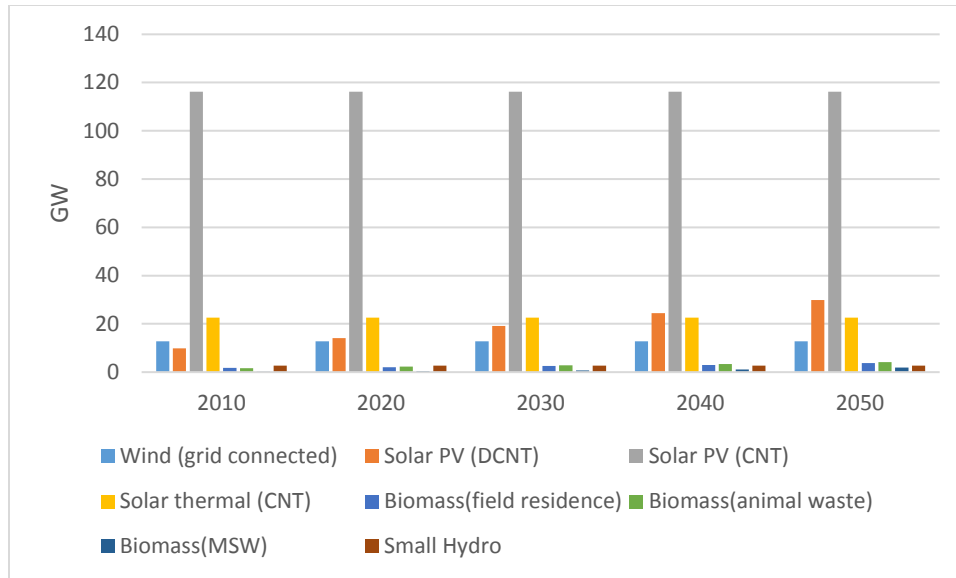


Figure 6: The estimated renewable energy potential [13]

Solar Photovoltaic potential is very high and it is around 118GW. Potential of wind is also reasonable and a few plants are being installed at coastal areas of Sindh. Biomass is also available throughout the country so wise use of biomass could help energy production in remote areas. MSW could also be used for energy production and it also has advantage that waste is properly disposed of due to which it causes reduction of environmental pollution [15]. The Pakistan Council for Renewable Energy Technologies (PCRET) was established in 2001 and objective of it was to research and develop the field of renewable energy in Pakistan. The main aim of PCRET is to develop clean and environmentally friendly energy resources and make its local fabrication feasible. Similarly, another department named as The Alternative Energy Development Board (AEDB) was established in 2003 by the Government of Pakistan and this act as the central national body related to renewable energy. The main objective of AEDB is to achieve the 10% share of the renewable technologies in the energy mix of the country [13].

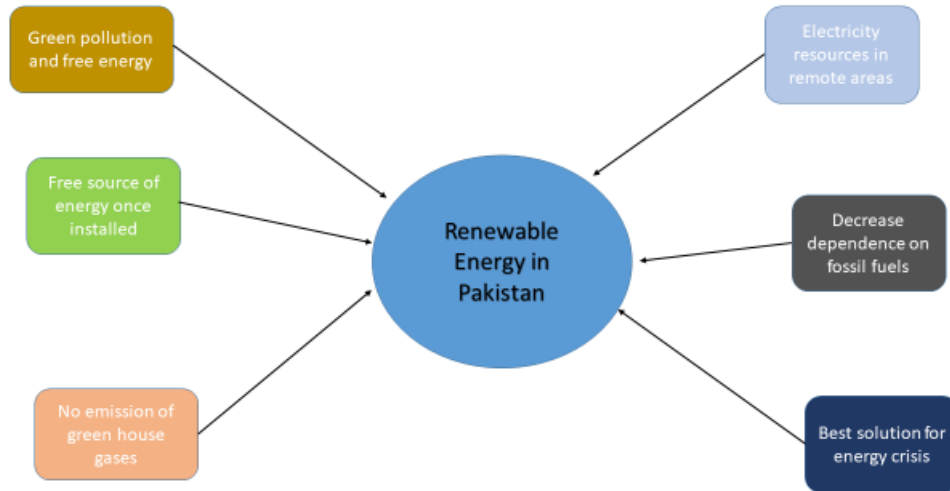


Figure 7: Advantages of renewable energy in Pakistan

The national renewable energy potential is about 167GW so there is need of proper planning to get benefit from these resources.

## 1.2 Fundamental working of Photovoltaic (PV)

Fusion reactions are taking place in the core of the sun. Energy produced on the sun is equivalent to 38,460 septillion watts ( $3.846 \times 10^{26}$  W) per second and temperature at the core of the sun is 15.7 million kelvins. Energy available at the surface of the atmosphere (at air mass 0) is  $1367 \text{ W/m}^2$  while on the surface of the earth (at air mass 1.5) is  $1000 \text{ W/m}^2$ . Water vapors, ozone, and dust absorb about 23% of the solar radiation. 71% of the solar radiations are being absorbed in the atmosphere and surface of the earth. This reduction of solar energy is due to reflection and scattering from  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{O}_3$ ,  $\text{NO}_x$  and dust particles. Absorption would be increased with the increase of path length. Light is being absorbed in PV solar cell as a result of which electron is being produced. Sunlight consists of photons. The energy of photon depends on the wavelength of the light. In the atmosphere, sun light is being absorbed like a black body. Absorption varies with wavelength and air mass.

A solar cell consists of two electrodes called anode and cathode. In typical silicon-based solar cell, PN junction plays a key role in the production of electrical energy. Silicon is n-type doped means

silicon is doped with a pentavalent atom like phosphorus due to which an excessive electron is being obtained. Due to the excessive electron, n-type atom is considered as a negative charge. P-type atoms are being obtained by doping silicon with trivalent atoms like boron due to which a vacancy is being produced. This vacancy is called hole and due to this doping p-type atoms are considered as a positively charged atom.

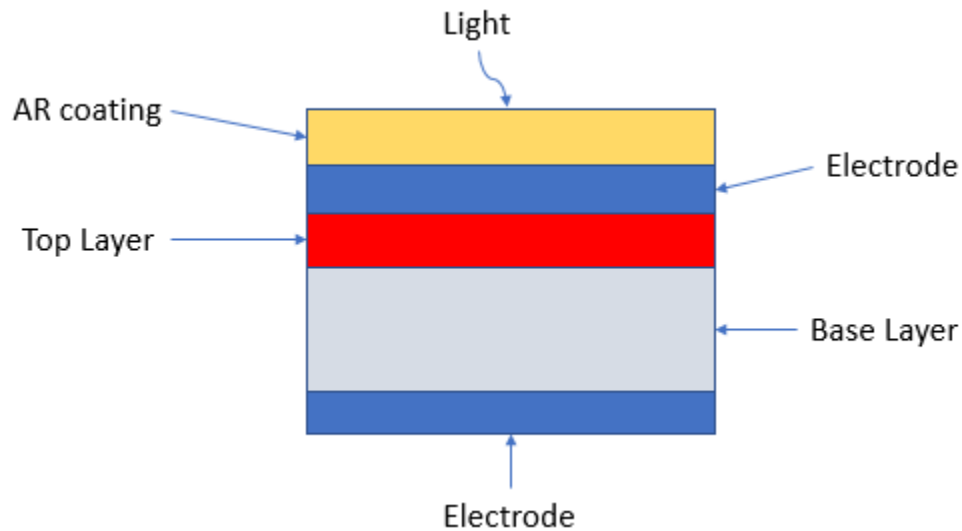


Figure 8: Structure of a typical solar cell

Above structure is a typical structure of a solar cell. Light fall on the solar cell. An anti-reflective coating is being deposited on the solar cell so that maximum light could be absorbed in the solar cell. Maximum light could be trapped which means output could be maximized. The base layer and top layer are basic solar cell with electrodes are on both ends. One electrode is called anode while other is called cathode. These contacts are ohmic contacts.

In a solar cell, there are basically four steps required for photovoltaic energy conservation

1. Light is being absorbed in semiconductor which gets excited from ground to excited state.
2. Atom in the excited state is converted into negative and positive charge.
3. Positive and negative charges move to respective electrodes. Negative charges move towards the cathode and positive charge towards the anode.
4. These charges move to an external circuit and then get combined by completing the circuit.

Electric current will be produced and the excited atom will move to the ground state.

A photon which falls on the surface of the solar cell has a specific energy. The energy of the photon depends on the wavelength of the light. Energy is inversely proportional to wavelength.

$$E = hc/\lambda$$

where

h is planks constant

c is speed of light

$\lambda$  is wavelength of light.

We want solar photovoltaic cell which could trap maximum wavelength range of light.

The maximum power output of the solar cell depends on the maximum output voltage, short circuit current and fill factor of the solar cell. Fill factor is ideality factor of the solar cell.

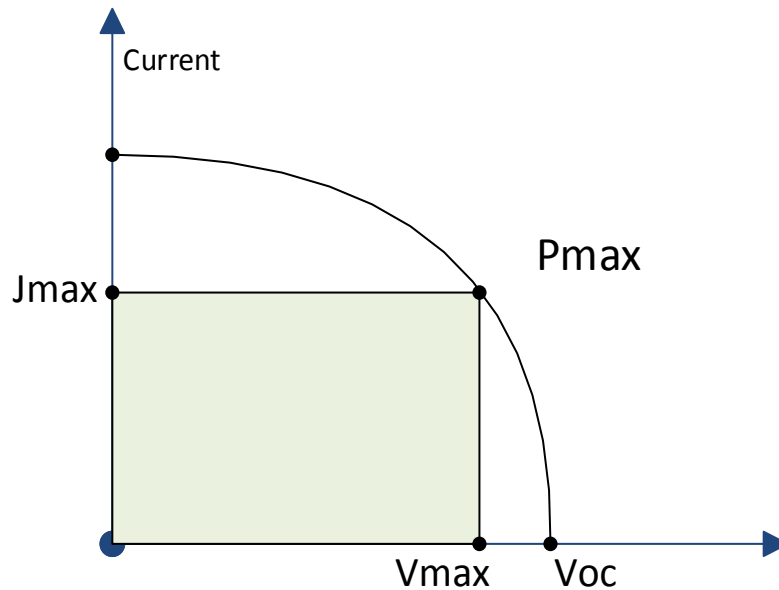


Figure 9: Current-voltage curve of a solar cell

$V_{oc}$  is open circuit voltage of the solar cell which is the maximum output of a solar cell.

$J_{sc}$  is short circuit current which is the maximum output of the solar cell.

Electric output Power is the product of voltage and current.

It depends on the product of current and voltage at every point on the graph. Power reached at a maximum point and voltage at that point is called  $V_{max}$  and current at that point is called  $J_{max}$ .  $V_{max}$  and  $J_{max}$  are not maximum values of the voltages and currents but these are the values at which maximum power is being attained from the solar cell.  $P_{max}$  is maximum output power which we can attain from solar cell.

$$P_{max} = V_{max} \times J_{max}$$

$P_{max}$  is being calculated through maximum power point tracking (MPPT). MPPT works on an algorithm in which at every point on graph power is being calculated by multiplying voltage and current on that point of IV curve. Power at next point is being calculated and then being compared with previous value and the maximum value is being tracked. Fill factor is the ratio of maximum attainable power to the product of  $V_{oc}$  and  $J_{sc}$ .



$$FF = \frac{V_{\max} \times J_{\max}}{J_{sc} \times V_{oc}}$$

Value of fill factor varies between 0 and 1. The best solar cell is one with maximum fill factor. Generally, fill factor varies between 0.4 and 0.75.

$$\eta = \frac{V_{\max} \times J_{\max} \times FF}{P_{in}}$$

The ideal maximum power is the product of  $I_{sc}$  and  $V_{oc}$

$P_{in}$  is  $1 \text{ kW/m}^2$  or  $100 \text{ mW/cm}^2$  which is solar irradiance on the surface of the solar cell. This is sun light intensity per unit area. Here area is active area on which sun light is falling.

The efficiency of the solar cell depends on ratio of the maximum power which is being drawn from solar cell to the power of the photon or light on the surface of the solar cell. The efficiency of the solar cell varies depending on the type of solar cell, the structure of the electrodes, aging factor and changes of the cell efficiency with time. Solar cell efficiency also varies with a change in temperature because high-temperature effect movement of electron thus reducing the efficiency of the solar cell. High temperature also deteriorates the aging factor of the cell and make a solar cell and its packing unstable.

### 1.3 Generations of solar cells

Three generations of photovoltaic solar cells have been commercialized while the fourth generation solar cell is still in research phase. Fourth generation solar cell are a polymeric solar cell.

### **1.3.1 First Generations solar cells**

First generation solar cells are normally silicon based solar cells. Crystalline Silicon based solar cells normally have 15%-20% efficiency. These are very stable solar cells but technologies used for fabrication of first generation solar cells are very energy intensive so these was need of less energy intensive technologies for fabrication of solar cells. Secondly, cost of first generation solar cells is very high because highly purified silicon is very rare and costly. These reason urged the need of new types of solar cells.

### **1.3.2 Second Generations solar cells**

Second generation solar cells are amorphous silicon and thin film silicon based solar cells. Efficiency of second-generation silicon solar cells are around 10%. These solar cells are easy to fabricate as compared to first generation solar cells.

### **1.3.3 Third Generations solar cells**

Third generation solar cells are very important types of solar cells. These are thin film solar cell technology. These are CIGS, CdTe based solar cells. These also include photochemical solar cells and organic polymers based solar cells. Efficiency of these types of solar cells is up to 15%. These solar cells are very easy to fabricate and materials of these solar cells are in abundant. Multi junction solar cells are also third generation solar cells and these are most efficient solar cells. In third generation solar cells energy band gap can be engineered by changing the materials and varying the technology so large wavelength of light can be used effectively in third generation solar cells.

Multi-junction solar cells are important type of third generation solar cells. Multi-junction solar cells has highest efficiency solar cells and currently used in satellites. These are very costly but with improvement in technology, its cost will reduce. A triple junction solar cell is InGaP/GaAs/Ge. Efficiency of multi junction solar cells is high because large wavelength band is absorbed especially low wavelength. Energy is high in low wavelength because wavelength and energy is inversely proportional to wavelength. Thermal losses are less in multi junction solar cells. Two methods are used for combining multi junction solar cells. One method is physically

separate them and connected through metal contacts while second method is through tunnel junction.[16][17]

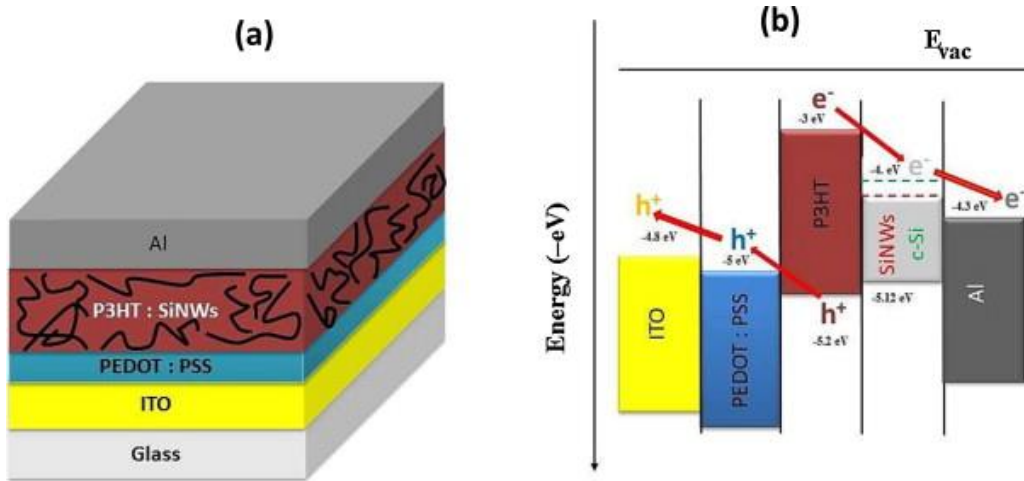


Figure 10: Multi junction solar cells [16]

Multi junction solar cell structure is shown in Figure above. This shows the band gap of different materials. Antireflection coating is on the top the top to maximize the light absorption.

Hybrid polymer solar cells are also types of third generation solar cells. Hybrid polymer solar cell consists of photoactive layers of two distinct chemical composition. One component is inorganic nanoparticle (NP) while other is organic semiconducting polymer.

The structure of hybrid solar cells is shown in Figure above. This is hybrid solar cell based on silicon nanowire and P<sub>3</sub>HT. Composition of Silicon nanowires and the solvent used for the film fabrication are very important for study of hybrid solar cells. Concentration of SiNWs is around 15%. The power conversion efficiency of these types of solar cells is around 0.10%.

Quantum dot solar cells are another important type of solar cells. In Q dot solar cell, light fall on transparent conducting electrode and it separate the electron hole pair. Q dot solar cells are high efficiency solar cells. Researchers are trying to improve the efficiency of solar cells and ultimate goal of efficiency is more than 60%. These are low cost solar cells and these can be fabricated by using low cost chemical processes like screen printing.

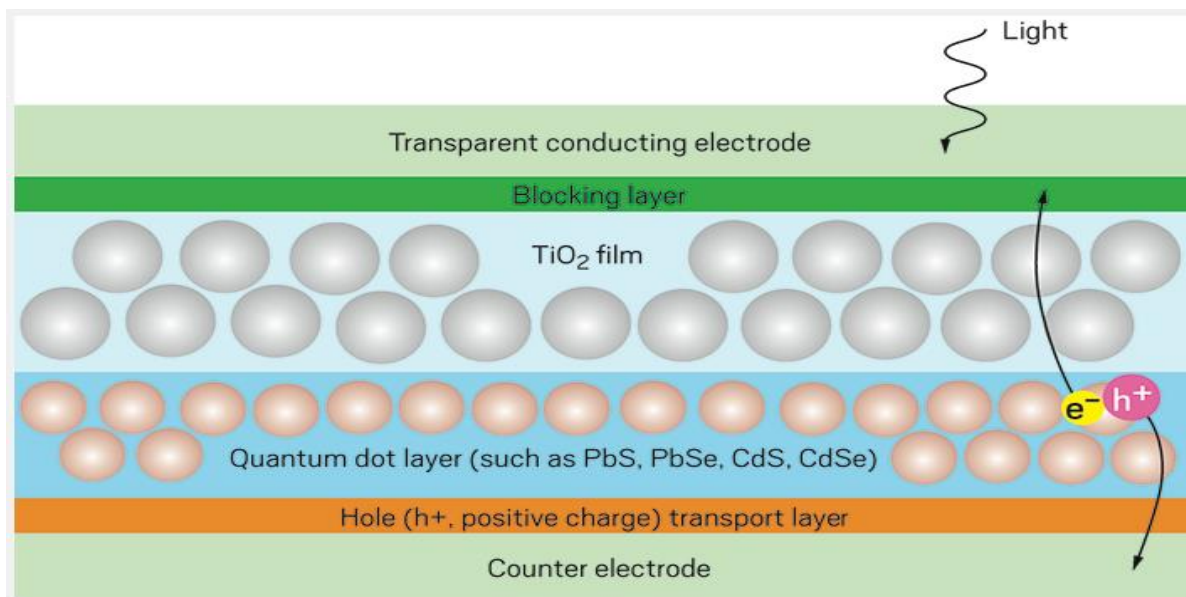


Figure 11: Working principle of Q dot solar cell [15]

Light fall on the transparent electrode of QDSC onto a photosensitive layer of dots leads to the formation of electron-hole pairs (e<sup>-</sup>/h<sup>+</sup>). One falling the photon or light, the charged particles

isolated and move to corresponding electrodes, thus producing electric current. Four-armed quantum dots solar cells are specific type of Q dot solar cells. In these solar cells, the specific shape of these crystals reduce the electron-hole pair recombination. Currently roll-to-roll printing technique and some other manufacturing techniques are being used for fabrication of Q dots solar cells [18] [19].

Perovskite solar cells are also another type of 3<sup>rd</sup> generation solar cells. The highest efficiency of Perovskite solar cells is 22.1%.

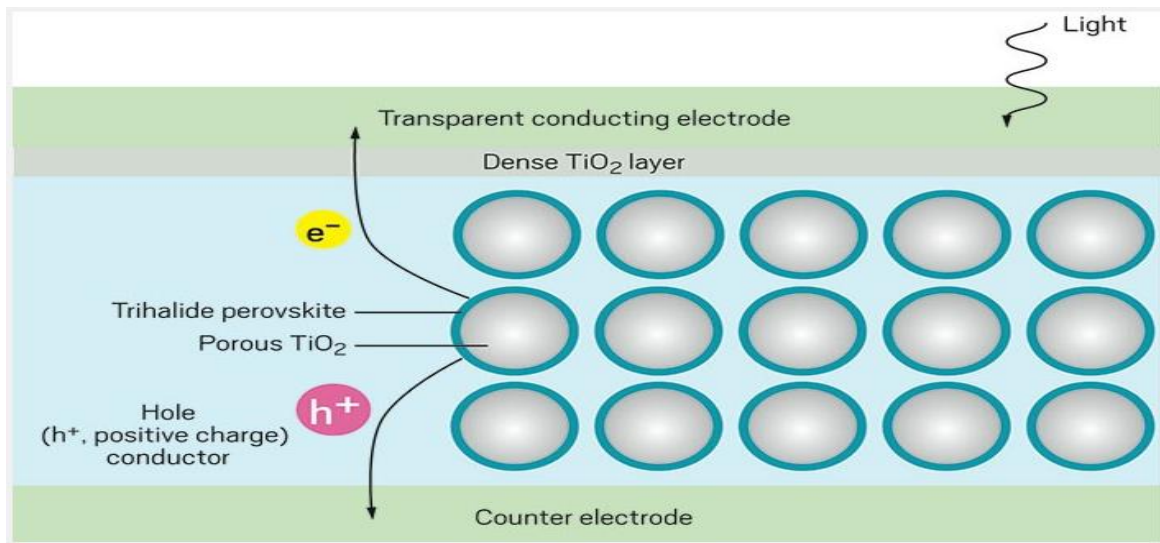


Figure 12: Working principle of Perovskite solar cells [17]

Perovskite solar cells use compounds with the perovskite crystal structure and structure of these solar cell is to absorb light.  $(\text{CH}_3\text{NH}_3)\text{PbI}_3$  is the highly studied material of Perovskite solar cells. The efficient movement of positive and negative generated by photoexcitation in Perovskite solar cells reach their respective electrodes so efficiently. In perovskite solar cell, light passing through the transparent electrode onto a layer of a photosensitive perovskite material and this stimulates excitations thus electron-hole pairs ( $e^-/h^+$ ) are generated. The charged particles are separated and diffused through the charge-conducting layers to respective positive and negative electrodes, as a result of which electricity is generated. Perovskite solar cells will be available for commercialization till 2021 and role of academic research will continue to play. The main

challenge in commercialization of perovskite solar cell is its stability. The light-sensitive material in this solar cell dissolves in the presence of water and unstable at high temperature.

Dye sensitized solar cells are third generation solar cells. DSSCs were invented by Professor Michael Grätzel and Dr. Brian O'Regan in 1991. DSSCs can be used indoor as well as outdoor to produce electricity. DSSCs use both natural and artificial light to produce electricity. Due to these qualities, DSSCs are being used for building-integrated photovoltaic (BIPV) applications. These also absorb wider range wavelength of sunlight as compared to silicon-based solar cells. Although the efficiency of DSSCs is less as compared to Silicon-based solar cell but with passage to time as research is going on DSSC, its efficiency is increasing due to discoveries in this field. The Dye sensitized solar cell is preferred over PN junction solar cell due to technological and economic advantages. The efficiency of DSSC was very low at the beginning but now it has reached up to 13% due to improvement in materials and deposition technique.

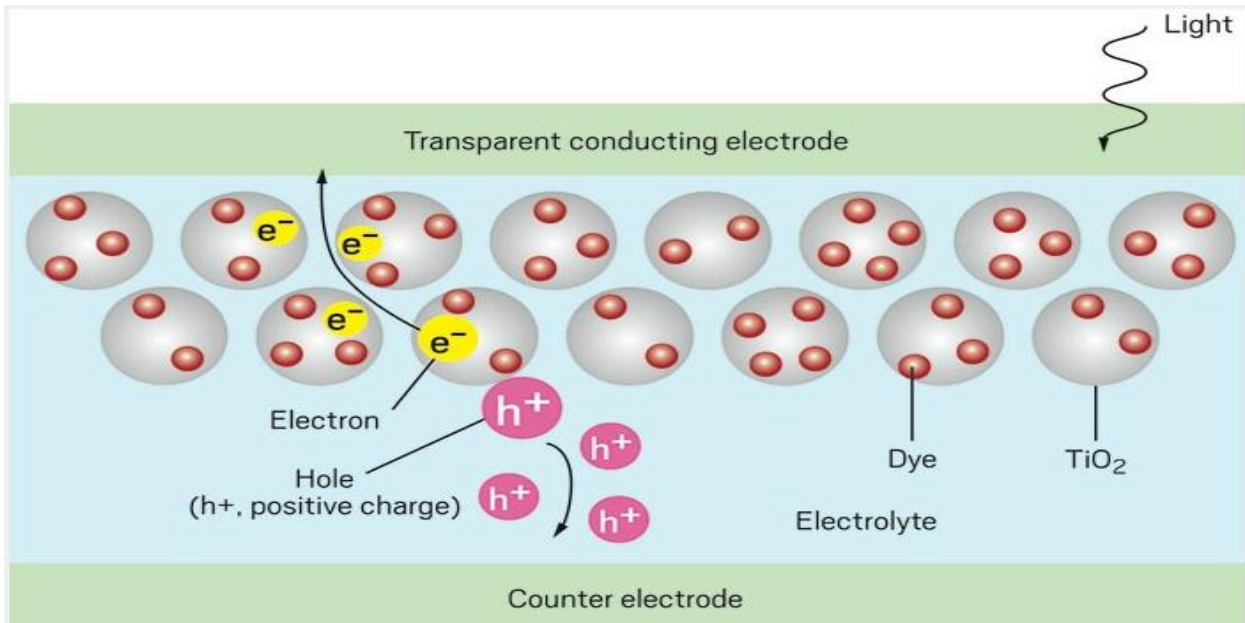


Figure 13: Working principle of DSSCs [18]

In silicon based solar cells and other conventional solar cells, light absorption, electronic excitation, and charge separation occur in a single layer of silicon but in DSSCs the events occur in separate molecular layers. DSSCs consists of a photoanode of titanium dioxide nanoparticles

that are coated with light-harvesting dye molecules and liquid electrolyte is used. The charges are separated at the surface of the nanoparticles and electrons are injected into the  $\text{TiO}_2$  layer and transported through  $\text{TiO}_2$  layer to photoanode. The positive charges move through electrolyte to the opposite side of the cell. The detailed working of the DSSCs is being discussed in next chapter.

## Chapter summary

Cheap and clean energy source is the most important need of humanity in modern era because energy production sources are polluting the environment. Renewable energy is best solution to tackle issue of the high energy production cost, depletion of fossil fuels and environmental pollution, energy production from renewable energy sources is increasing globally day by day. Solar energy is a cheap and most abundant form of renewable energy. Cost of solar energy is reducing day by day due to improvement in efficiency of solar cells. In solar energy, light falling on the surface of the solar cell excite the atoms of the solar cell and electron is emitted when this atom comes back to ground state. Electron hole pairs are generated as a result of sun light. Efficiency of solar cell depends upon open circuit voltage, short circuit current and fill factor.

There are multiple types of solar cell like silicon solar cell, hybrid solar cell, Q dot solar cells, perovskite solar cells, multilayer solar cell and dye sensitized solar cells. Dye sensitized solar cell is major focus in this research work. It is organic solar cell consists of photo anode, counter electrode and an electrolyte.



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# Chapter 2: Literature review

Dye sensitized solar cells are gaining high importance with improvement in efficiency and with new innovative materials. In this chapter, importance of DSSC and its detailed working is being discussed. In my research, I have selected the suitable material which can act better as counter electrode for DSSCs. Carbon nano-materials are preferred materials for counter electrode of dye sensitized solar cells. Metal oxide composite is prepared with CNTs to improve the conductivity of the counter electrode for DSSCs. NiO nano-materials are prepared by catalytic chemical vapor deposition process. Similarly CNTs are purified by using chemical vapor deposition process. NiO-CNTs composite is prepared by using co-precipitation method. SEM analysis is performed on all three samples. Similarly XRD analysis is also performed for all three samples. Results are also discussed in detail. Solution of these materials are prepared and coated on ITO coated PET using spin coating techniques. Coated samples are characterized using Hall Effect equipment technique and cyclic voltammetry analysis. Complete DSSC is fabricated using microfluidic analysis technique. Efficiency of all these solar cells are obtained using IV profiling technique. Comparison of Voc, Isc, FF and efficiency is being made between all three DSSC.

## 2.1 Dye sensitized solar cells

Dye sensitized solar cells are third generation solar cells. DSSCs were invented by Professor Michael Grätzel and Dr. Brian O'Regan in 1991. DSSCs can be used indoor as well as outdoor to produce electricity. DSSCs use both natural and artificial light to produce electricity. Due to these qualities, DSSCs are being used for building-integrated photovoltaic (BIPV) applications. These also absorb wider range wavelength of sunlight as compared to silicon-based solar cells. Although the efficiency of DSSCs is less as compared to Silicon-based solar cell but with passage of time as research is going on DSSC, its efficiency is increasing due to discoveries in this field. The Dye sensitized solar cell is preferred over PN junction solar cell due to technological and economic advantages. The efficiency of DSSCs was very low at the beginning but now it has

reached up to 14% due to improvement in employed materials and the deposition techniques [1]. The Figure 14 shows the number of research papers published each year in journals [2].

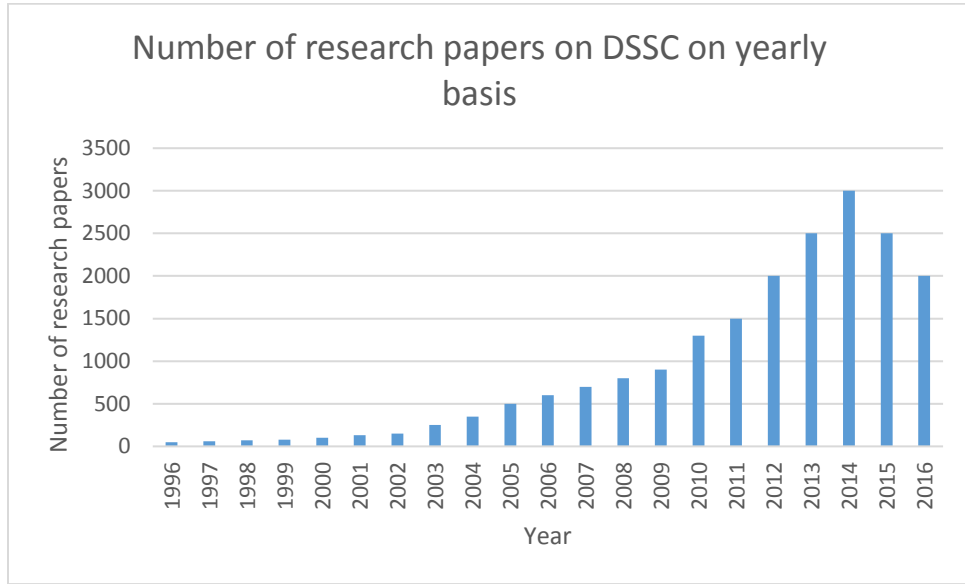


Figure 14: Number of Research papers in each year

A comparison has been made for a few factors between semiconductor based solar cell and dye sensitized solar cell and reported in the table 1.

Table 1: Comparison between semiconductor based solar cell and Dye sensitized solar cell

<b>Comparison Factor</b>	<b>Semiconductor based solar cell</b>	<b>Dye sensitized solar cell</b>
Power generation cost	High cost	Low cost
Transparency	Opaque	Transparent
Material's behavior towards Environment	Normal	Highly friendly
Power generation efficiency	Better	Normal
Color	Few	Multiple

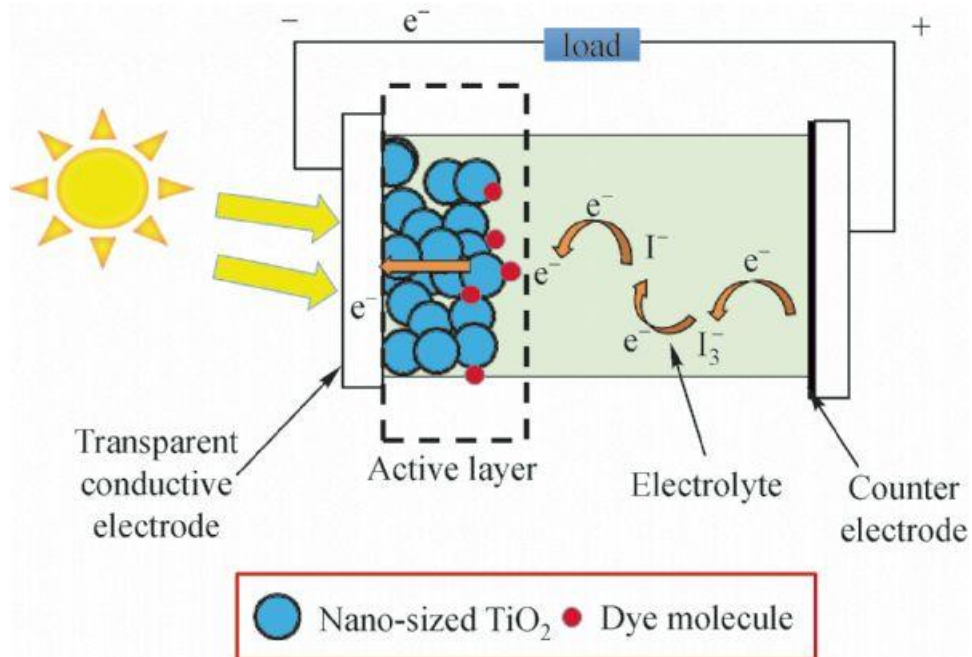


Figure 15: Structure of DSSC

## 2.2 Structure of Dye sensitized solar cell

DSSC is being called so because in this cell an organic material (dye) is being sensitized and this is a basic principle of the solar cell. The dye in dye sensitized solar cell replaces light absorbing pigments (chlorophylls), similarly, nanostructured semiconductor layer replaces oxidized

NADPH and carbon dioxide acts as the electron acceptor. The electrolyte in DSSC acts as the water in leaf while oxygen as the electron donor and oxidation product.

DSSC consists of main four parts

- I. Photo Anode
- II. Dye
- III. Electrolyte
- IV. Counter electrode

### 2.2.1 Photo Anode

Photo anode consists of a transparent conducting oxide (TCO) glass with a resistivity of few ohms. Normally one side of the glass is coated with a layer of fluorine-doped tin dioxide (FTO) or indium-doped tin oxide. Semiconductor nanoscale material is being coated on this conducting side of the glass. Photo anode should be designed to have a larger surface area so that maximum light could be trapped. Light absorption is dependent on the surface area of the photo anode. Nano structures are being prepared to maximize the surface area and light trapped. Initially,  $\text{TiO}_2$  was being used as semiconductor nanomaterial but now  $\text{SnO}_2$  and  $\text{ZnO}$  are also being used as semiconductor nanomaterial.

#### 2.2.1.1 $\text{TiO}_2$ Photo anode

Titanium oxide is photo catalyst material and it has the features of high conductivity, low cost, found abundant in nature and environment-friendly due to non-toxic behavior. It also has an advantage that it can absorb wider band gap of ultraviolet light. The transition of few metal ions (Fe, Fe, Cr, Co, Mn, V, Mo) with  $\text{TiO}_2$  engineered the band gap of  $\text{TiO}_2$ . Transition of these metals reduces the energy band gap thus the number of photons being absorbed is increased. A few non-metal ions (B, C, N, S, F) are also being doped with  $\text{TiO}_2$  to enhance its photo catalytic activity. Similarly, Sulphur is also being doped with  $\text{TiO}_2$  to capture the maximum spectrum of light. Hydrothermal, sol gel and solvothermal process are being used for doping of ions with  $\text{TiO}_2$ . The ultimate purpose of this doping is to utilize the light below visible region. This spectrum of light has high energy so by capturing this useful portion of the light spectrum could enhance the efficiency of DSSCs [3].

#### 2.2.1. 2 $\text{ZnO}$ photo anode

$\text{ZnO}$  nano material is also being used as photo anode for dye sensitized solar cells. This material has higher surface area and thus it can absorb a large amount of light. Nano rods structures are being made through  $\text{ZnO}$  thus these nano rods cause an increase in surface area due to which efficiency is increased. The efficiency of DSSC depends on the size of the nano rods of  $\text{ZnO}$  [4].  $\text{ZnO}$  is also being deposited on transparent conducting oxide glass as nano flowers by using

hydrothermal process. The efficiency of DSSC based on ZnO nano flowers is around 1.9% while the efficiency of ZnO nano rods is around 1% thus nano flowers have higher efficiency than ZnO nano rods [5]. Sol-modified ZnO is also being used as photo anode for dye sensitized solar cell. Sol-modified ZnO photo anode shows 39% higher efficiency than unmodified ZnO photo anode for dye sensitized solar cell. Due to sol-modification process crystallite diameter increased from 15.1nm to 18nm. Short circuit current also increased by 46% [6]. ZnO nanowire is also being used as photo anode for dye sensitized solar cells. ZnO nanowires are grown on FTO coated glass using chemical bath method.

### **2.2.2. Dye:**

Dye could be made from organic or inorganic chemicals. Dye should have wide range absorption, high absorption coefficient, high anchoring property, high stability and optimum redox potential. Dye is being used to absorb light. Ruthenium dye was being used initially but now several dyes are being used including an organic and inorganic dye. Dye is being absorbed on photo anode [7]. There are mainly two types of dyes synthetic dyes and organic dyes. Organic dyes are easy to fabricate from natural resources while synthetic dyes are fabricated by the complex fabrication process. There are multiple factors on basis of which we analyze dye and their role in dye sensitized solar cells [8]. Synthetic dyes are higher in cost as compared to the cost of organic natural dyes due to the higher cost of material involved in reactions during fabrication of synthetic dyes. Organic dyes are better on basis of environmental benefits as compared to synthetic dyes. Stability of organic dye is much better as compared to the stability of synthetic dye. The absorption spectrum of synthetic dye is higher as compared to organic dye. The absorption spectrum of synthetic dye is up to 800 nm while absorption spectrum of the organic dye is 400 nm-700 nm. The efficiency of synthetic dye is much higher than an organic dye. Organic dyes are easily available while synthetic dyes are hard to manufacture. Similarly, organic dyes can be manufactured easily but synthetic dyes require a variety of solvents and also time-consuming so now focus is to improve the efficiency of organic dye [9]. There are few commonly used dyes for example, ruthenium (Ru) bipyridyl derivatives (N3: cis-diisothiocyanato-bis (2,20-bipyridyl-4,40-dicarboxylic acid) ruthenium(II), N719: di-tetrabutylammonium cis bis(isothiocyanato)bis(2, 20-bipyridyl-4,40-dicarboxylato) ruthenium(II); Z907: cis-bis (isothiocyanato)( 2,20-bipyridyl-4,40-dicarboxylato)(4,40-di-nonyl-20- bipyridyl) ruthenium(II)) [2]. Dye is absorbed on surface photo

anode. Photo anode is dipped in a solution of the dye. Dye is absorbed in ethanol and in this solution, TiO<sub>2</sub> coated FTO glass is dipped in a beaker [10]. Photo anode which is an electrode consists of TiO<sub>2</sub> coated FTO glass and adsorbed dye. The thickness of the dye is around micrometer. There are main three main factors on which nature of dye depending on, for example, polarity and types of substituents due to which dye interacts with TiO<sub>2</sub> layer. PH of the dye is also important and it also affects the overall efficiency of solar cell.

### **2.2.3 Electrolyte**

The electrolyte is a pathway for an electron from the counter electrode to photo anode. It should have made from stable redox material. It should have optimum redox potential, high stability, good solvent and high interaction with dye. Initially, the liquid electrolyte was being used but now gel and solid hole conducting electrolyte are being prepared. Electrolytes are organic as well inorganic solvents. The efficiency of DSSCs based on organic solvents liquid electrolytes such as acetonitrile (AN) have efficiency around 11% [11]. There are few problems with a liquid electrolyte that liquid electrolytes are volatile and these can get a leak from dye sensitized solar cells so there is need of nonvolatile electrolytes. The viscosity of electrolyte is also very important because diffusion of redox couple ( $I^-/I^3$ ) is dependent on the viscosity of electrolyte [12]. The organic hole transporting material, inorganic semiconductor material, and polymer electrolytes are a better replacement of liquid electrolytes to tackle above described issue [13].

There are few important materials like ethylmethylimidazolium-based ionic liquids (ILs) are a better replacement of conventional electrolytes but these materials are expensive and toxic so these can increase the cost of dye sensitized solar cells [14]. There is an innovative electrolyte which is quaternary ammonium salt-derivative ionic liquid called G.CI. This is a mixture of glycerol and choline iodide to form electrolyte for DSSCs. The efficiency of G.CI electrolyte based dye sensitized solar cells is around 3.1% [12]. These are preferred because these are easy to prepare [11] [14]. The polyhedral oligomeric silsesquioxane (POSS) is also used as an electrolyte for DSSCs and this is solid state electrolyte. The POSS grafted with the methyl-substituted imidazolium show the maximum efficiency of 6.52%. The temperature of the electrolyte was previously 5-6°C but now in latest research temperature is being dropped to -8.8°C due to which maximum conductivity is achieved. The conductivity of POSS electrolyte is very important as its conductivity directly affect the efficiency of DSSCs [15].



#### 2.2.4. Counter Electrode

Counter electrode can be made from metal and non-metal. The counter electrode should have a high surface area, high stability, and high catalytic activity. Traditionally counter electrode is being prepared with platinum. Platinum is being used due to its high conductivity. There is still an issue that platinum is not stable with electrolyte so there is a need for stable and low-cost material. There are multiple materials which can be used as a counter electrode for dye sensitized solar cell.

##### 2.2.4.1 Platinum as a counter electrode

Platinum is highly conductive rare earth metal. It is being preferred as a counter electrode due to its high catalytic activity towards  $I_3^-$  and low charge transfer resistance. The thickness of platinum on the conductive glass is also very important and it should be around 0.2-2 micron. There are multiple deposition techniques like electrochemical deposition and thermal vapor deposition. Transparent platinum is stable and this is used as a counter electrode due to the high surface area and high catalytic activity. The transparent platinum thin film is also being used for back-side illumination. Platinum nano particles counter electrode has much better performance than bulk platinum counter electrode based solar cell [16]. Platinum composites are also being used as a counter electrode for DSSC. Graphene- platinum composites are also very conductive and show much better performance and simple platinum metal based counter electrode for DSSC.

##### 2.2.4.2 PEDOT: PSS counter electrode

PEDOT: PSS has got much reputation during this decade. PEDOT: PSS is highly conductive material. PEDOT: PSS liquid is being added to organic solvents like dimethyl sulfoxide, N, N-dimethyl acetamide (DMAc), DMF and dichloromethane (DMC). To further increase the roughness and conductivity of the PEDOT: PSS, carbon black or CNTs is added. Dip coating and spin coating techniques are used to deposit polymer on FTO glass. DMSO-PEDOT: PSS (C: 2.0 wt.%) shows maximum conductivity and conductivity of this sample is 350 S/cm [17]. The efficiency of DMSO-PEDOT: PSS (C: 0.1 wt.%) is 5.81% and this efficiency is comparable to the efficiency of platinum (5.61%) based counter electrode for DSSC. The thickness of the PEDOT: PSS is in micrometers. The number of polymerization cycles is being used to control the thickness

of the PEDOT: PSS. The efficiency of DSSC varies with the thickness of the polymer. Polyvinyl propylene and graphene powder are also being added to PEDOT: PSS. PVP and graphene powder increase binding of carbon/PEDOT: PSS thus this increased conductivity of counter electrode and increase the efficiency of solar cell. This solution is being deposited through scratch method and thickness of solution is 3-4 micrometer.

#### 2.2.4.3 Carbon nano materials based counter electrode

Carbon nano materials have got much attraction due to high strength, high electrical conductivity, low cost and high catalytic activity towards triiodide ion. There are multiple forms of carbon nano materials like carbon black (CB), carbon nanotubes, single-walled carbon nanotubes, multiple walled carbon nanotubes carbon nano fibers and NiO-CNTs.

Carbon black is formed by incomplete combustion of organic petroleum product. Active sites are available at the crystal edge of the carbon black. The thickness of carbon black layer is very important and fill factor of solar cell increase with a thickness of the counter electrode. Charge transfer resistance also reduces with an increase of the thickness of the counter electrode [18].

Carbon nano fibers (CNFs) have a diameter of 10-80 nm and it plays an important role as a counter electrode for DSSC. Carbon nanofibers are being synthesized by catalytic decomposition process. Carbon nanofibers are also being prepared by electrospinning of polyacrylonitrile (PAN) which has high conductivity. Similarly, poly vinyl propylene is also used for carbon nanofibers. Nanofibers are being prepared through pyrolysis. Pyrolysis is carried out at 900°C in nitrogenous environment. The carbonized carbon nanofibers are also being prepared by carbonization process. Electrospinning technique is used for deposition of PAN and PVP. Carbon nanofibers are prepared in electrospinning process through strict control on feed rate, the voltage applied, distance from charged plate and viscosity of the fluid. After deposition electrode is dried at a different temperature varying from 400°C to 750°C. CNFs dried at 550°C show lowest fill factor but highest efficiency. The efficiency of carbon nanofibers is still less then the efficiency of carbon black. Efficiency of DSSC is highest for 50-micrometer thickness [19]. There is also a type of carbon nanofibers called vertically aligned carbon nanofibers (VACNFs). VACNFs structure is highly conductive structure and this is needle-like structure and core-shell structure. The diameter of VACNFs is controlled to be 50nm-100nm. VACNFs show efficiency of 1.5% [20].

Polyvinyl alcohol is a water-soluble polymer. Polyvinyl alcohol has a melting point of 180°C-190°C. This has a degree of hydrolysis of 86.5%-89%. PVA is non-toxic so it can be used without hazardous fear. Concentration range of PVA is 1000-20,000 mg/l. Polyvinyl alcohol is also used for dispersion of carbon nanotubes. Single-walled nanotubes macro films are used as a counter electrode for DSSCs. CuNi NPs are deposited through electrospinning technique and then calcination. PVA is used for decomposition of carbon nanomaterials and metallic acetate. These nanofibers are used as a counter electrode for DSSCs [21] [22]. Polyvinyl alcohol is preferred due to low cost and better conductive properties [22]. PVA is also used to disperse MWCNT and the main advantage is that it evaporate at room temperature [23]. PVA-MWCNTs are also used for cholesterol level detection through injection of microfluid. 1wt% PVA is used for dispersion of CNT-COOH. Thin films are being deposited on conductive glass [24].

Polyvinyl pyrrolidone is used as a polymer for dispersion of carbon nanotube for fabrication of counter electrode for dye sensitized solar cell [25]. PVP is soluble in water and also in polar solvents but this is not soluble in esters, ethers, ketones and hydrocarbons [26]. This polymer is non-toxic and this form highly conductive film when deposited on a substrate. In this experiment, Polyvinyl pyrrolidone is dispersed in DMSO and then this solution is mixed with CNTs dispersed in DMSO. Polyvinyl pyrrolidone with the average molecular weight of 40,000 manufactured by Sigma Aldrich is used in the experiment.

Multiwalled carbon nanotubes and single-walled carbon nanotube are also important forms of carbon nanomaterials which are being widely used for a counter electrode for dye sensitized solar cells. SWCNTs and MWCNTs are highly conductive materials and also highly stable towards redox reaction. SWCNTs and MWCNTs have high mobility, high conductivity, mechanical strength and optical strength. These can be dissolved in organic solvents easily and thin films of this material can be formed easily as well [27]. SWCNTs have a diameter in the range of few nanometers while the diameter of MWCNTs is tens of nanometers. Best efficiency is being achieved of SWCNTs (3 wt.%) is around 1.3% and fill factor of .55 [27]. Reduced graphene oxide (rGO) is also being added to single-walled carbon nanotubes.

#### 2.2.4.4 Metal oxide as counter electrode

Pseudo capacitance has been studied of many metal oxides. NiO has a special importance among these metal oxides due to its easy availability, environmentally friendly, low cost, and high pseudo

capacitive behavior [28] [29]. NiO-CNTs are important due to better pseudo capacitive properties containing faradaic redox reactions, which occur within the active electrode materials. NiO-CNTs are Nano materials and have large surface area. Electronic conductivity of NiO-CNTs is much better as compared to NiO and CNTs alone. Functionalization of CNTs with negatively charged PSS can large number of electroactive sites that can bind ions with positive charge oriented growth of metal oxide along the CNTs.

### 2.2.3 Working principle of dye sensitized solar cell

Dye sensitized solar cells work on same principle as photosynthesis of plant. In DSSCs product is electrical energy instead of glucose. Working principle of DSSC is shown in diagram below.

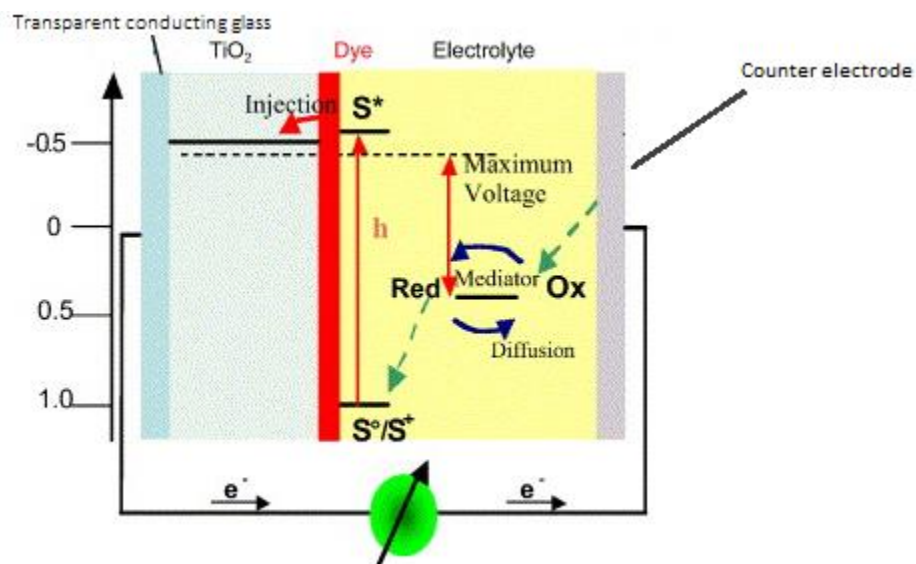
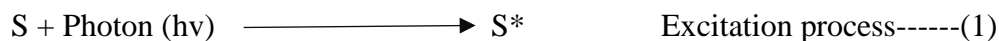


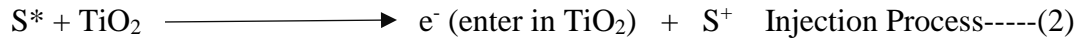
Figure 16: Working diagram of Dye sensitized solar cell [30]

The basic working principle of DSSC consists of the following steps.

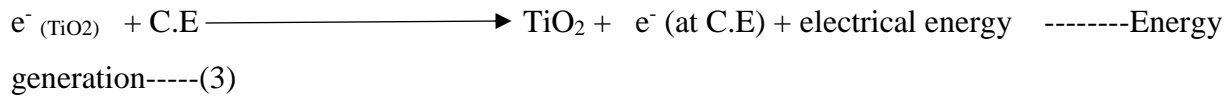
When Light falls on the DSSC, photon absorbs in dye, it excites the electron. An electron moves from HOMO (highest occupied molecular orbital) to LUMO (Lowest unoccupied molecular orbitals) by obtaining the energy of the photon ( $h\nu$ ).



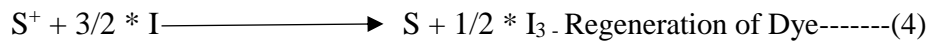
Photon is absorbed in dye and it excites the dye. The dye absorbs all photons of the energy of energy difference between HOMO to LUMO. An electron from grounded state get excited to excited state this is called photo excitation. An electron in LUMO is not stable as LUMO is an unstable state.



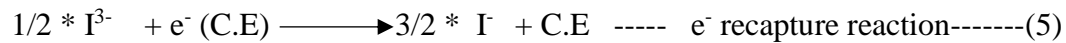
From LUMO excited electron is injected into TiO<sub>2</sub>. Fermi level of the TiO<sub>2</sub> should be less than LUMO of Dye.



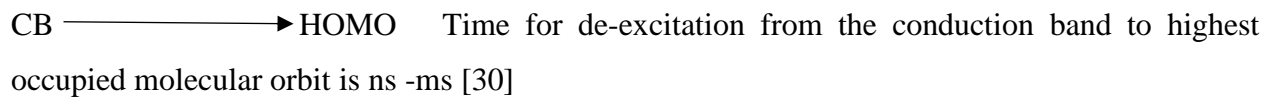
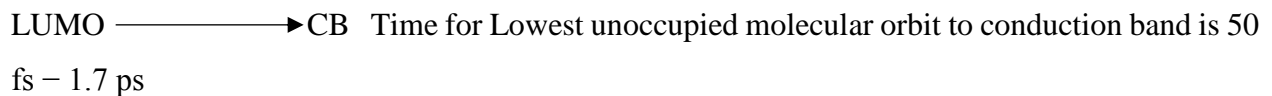
Then electron injected to TiO<sub>2</sub> and move to counter electrode. Here holes are being blocked the only electron are injected to TiO<sub>2</sub> layer. Injection time is about 10<sup>-15</sup>-- 10<sup>-12</sup> sec.



Electrolyte oxidizes the Dye. Electrolyte consist of Iodide ion. Dye react with I<sup>-</sup> and Dye is regenerated.



At counter electrode, electron reacts with tri-iodide ion due to which iodide ion is regenerated which is reused in the regeneration of Dye. This is a complete cycle of electricity generation in DSSCs.



In electrolyte



From above diagram, this is clear that dye is being regenerated and similarly electrolyte also come back to its original state [31].

Besides these reactions, at different interfaces of dye sensitized solar cell multiple recombination reactions take place and due to recombination efficiency of solar cell is being reduced. There are two main interfaces at which recombination take place.

- I. At the interface between the conduction band and  $\text{TiO}_2$ .
- II. In electrolyte through counter electrode and triiodide ion.

The recombination rate is slow thus solar cell working is kinetically feasible. Thus the ultimate task is to reduce recombination rate so that solar cell could be made more efficient.

## Chapter summary

Dye sensitized solar cells are very important solar cells due to their low cost, better efficiency and less manufacturing equipment. DSSCs consists of photoanode, an organic dye, counter electrode and an electrolyte. ZnO nanowires are used for manufacturing of photoanode of DSSCs. Dye is used to absorb the sun light falling on the surface of the solar cell. Organic dye are getting attention due to better performance and low cost. POSS, N 3 and N 719 are dyes used in DSSCs. Dye is absorbed on Titania deposited FTO glass. Electrolyte is a pathway for electron from counter electrode to photoanode. Electrolytes are solid, liquid and gel form. Electrolytes are organic as well as inorganic. Counter electrodes are made from metal as well as nonmetals. Traditionally platinum is used for fabrication of counter electrode but platinum is rare earth metal and expensive metal so there is need of a cheap metal to fabricate the counter electrode. Carbon nanomaterials is highly conductive and to further improve the conductivity of the carbon nanomaterials, metal oxide like NiO composite is used with carbon nanomaterials. NiO-CNTs composite is a better replacement of platinum as counter electrode for DSSCs.

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# Chapter 3: Introduction to experimental and characterization techniques

There are multiple techniques involved in manufacturing of materials for solar cell fabrication. Similarly, multiple characterization techniques are being discussed in this chapter.

## 3.1. Deposition technique for counter electrode

There are multiple techniques used for deposition of conductive materials on the counter electrode for dye sensitized solar cells.

- I. Spin coating technique
- II. Electrospinning technique
- III. Chemical vapor deposition (CVD)
- IV. Doctor blade deposition technique

### 3.1.1 Electrospinning technique

In electrospinning technique, the conductive material is being deposited through charged deposition. Complex structures can be obtained through electrospinning techniques. The surface area of the deposited layer is higher in case of electrospinning technique. Nanofibers structures of diameter ranging from few nanometers to few micrometers are formed through electrospinning. In electrospinning nanofibers obtained have longest length. Due to electrospinning technique nano structural properties of solutions can be tested through Nano level fabrication. Over the past few years, more than 200 polymers were Electrospun for multiple purposes and much more are in process. The term “electrospinning” is being derived from “electrostatic spinning”. This technology was being initiated in 1994. In this technology, two electrodes with opposite charges are being applied. One electrode is being placed in polymer fluid which is in injection while another charge is applied on the charged plate. The solution is ejected from the needle as a charged particle. The applied potential difference depends on properties of solution, for example, the viscosity of the solution and molecular weight of the solution. The distance between electrodes is

also very important. When this distance is short, spun fibers stuck to collecting plate and also to each other due to incomplete evaporation. DC voltage applied can reach up to 30KV. There are total three basic components in electrosponner, high voltage supplier, a capillary tube of few millimeter diameter and a metallic collector. In few cases, metallic electrode is grounded or supplied with a negative charge. Value of negative charge can be controlled from a knob on the control panel.

The main parameters of electrospinning are further divided into further respective groups which are the following

#### Solution

- Viscosity of solution
- Molecular weight of polymer
- Conductivity of polymer
- Concentration of solution
- Solvent properties of the solution
- Surface tension

#### Process parameters

- Voltage applied
- Flow rate
- Capillary geometry
- Distance from the capillary tube from the collector

#### Atmospheric parameters

- Temperature
- Relative humidity

### 3.1.1.1 Working Principle of electrospinning

Electrospinning equipment available at USPCASE is FLUIDNATEK LE 10. The image of the equipment is given below.

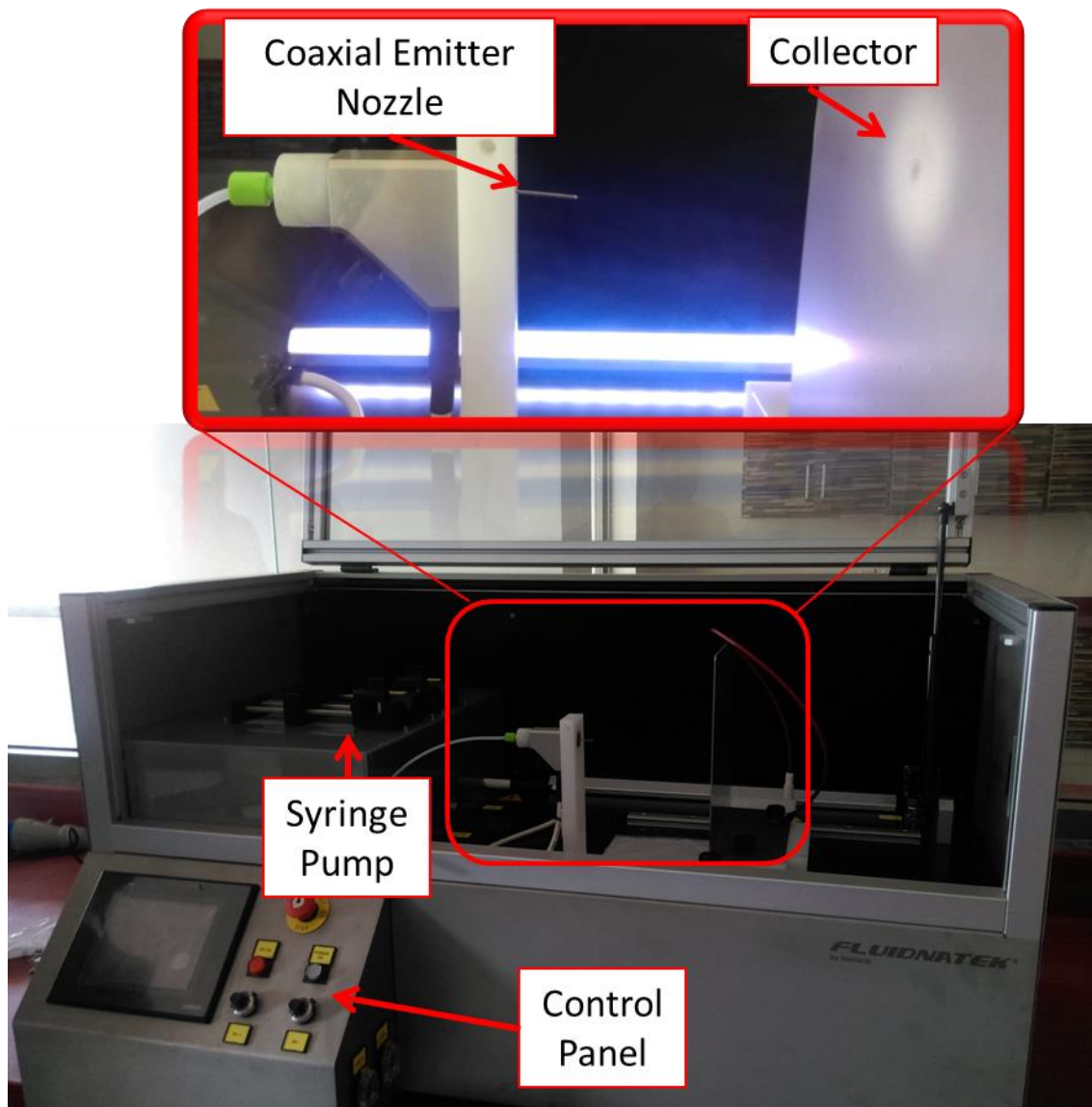


Figure 17: FLUIDNATEK LE 10 at USPCASE NUST

The FLUIDNATEK LE-10 is equipment working on the principle of electro-stretching or estretching technology. On Control panel there is a button and two knobs. Through control panel voltages applied can be varied and high voltage (HV) On button is also on the control panel. There is a button ON/OFF on back side of the electrospinner. Before switching on the equipment we have to make sure that collector HV socket which is shown in the Figure below is connected properly and connection plate is properly tightened through adjusting knob. The injection which can be seen in the Figure below should be placed properly and also should be tightened properly. In this equipment, it is possible to deposit two solutions simultaneously. There are two places for injection one is called Liquid-1 and Liquid-2. The flow rate of both liquids can be controlled through a button on the touch panel.

When we switch ON the equipment through ON/OFF button at the back side of the electrospinner. Then we have to switch on the high voltage equipment. Power on button is the control panel. When “power on” button is pressed HV indicator light switch on showing that high voltage is on. Voltage can be increased through knobs. Voltage should be increased slowly with the rotation of knob of injector potentiometer. Negative voltage potential can also be applied through collector potentiometer knob. The voltage applied is shown on screen (display) of electrospinner. Voltage should be kept below 30KV for the safe operation of the equipment. The flow rate is controlled through two flow controller button on touchscreen. [2]

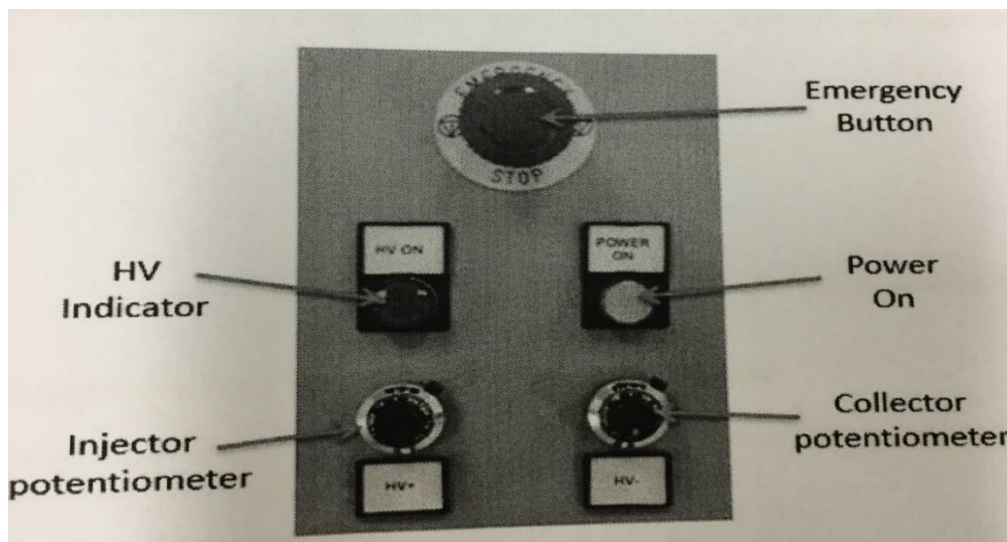


Figure 18: Control panel on electrospinner

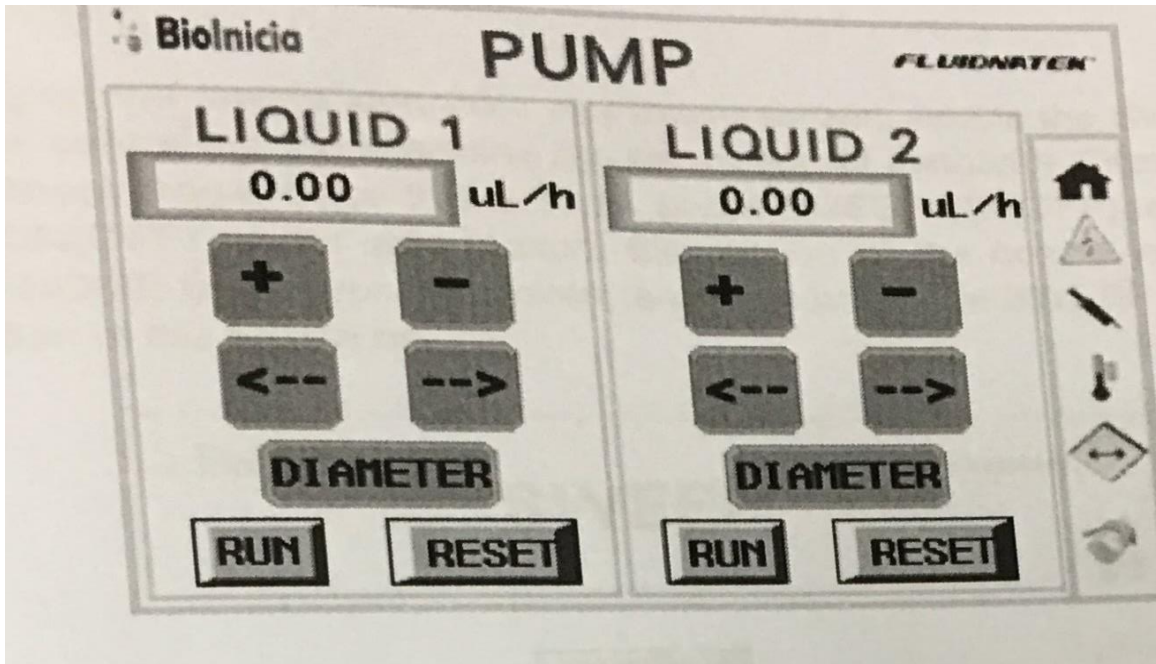


Figure 19: Flow rate control

### 3.1.1.2 Stepwise procedure of Electrospinning

There are multiple steps involved in electrospinning which are the following

1. Before switching on the equipment make sure that solution is filled in a syringe and all connections are properly installed.
2. Make sure that conductive glass (FTO coated glass)/ITO coated PET is attached on the conductive plate.
3. Switch on the equipment and on the high voltage button.
4. Rotate the knob to increase the voltage until reaching the desired voltage
5. After reaching the required voltage, start the flow of the fluid by setting the flow rate and pressing the RUN button on touchscreen.
6. Fluid will start coming out of the syringe and it will be in form of a jet.
7. Voltage is adjusted to make sure that taylor cone of the solution is formed properly.
8. Nanofibers will start depositing on the conductive glass.
9. Make sure that thickness of the thin film is enough so that it could work as counter electrode properly.



10. When the experiment is completed, decreased the voltage slowly by rotating the voltage knob.
11. Switch OFF the equipment from ON/OFF button and unplug the equipment.
12. Detach the glass/ sheet from conductive plate.
13. The counter electrode is tested by using SEM, XRD, AFM and Hall Effect.
14. The complete cell is fabricated by using micro fluidic technique.

### 3.1.2 Spin coating

Spin coating is another important technique used for deposition of the solution on glass/sheet. In this coating equipment, the vacuum pump is used to hold the substrate on which deposition is to be done. The substrate is placed on the rotating chunk and this chunk rotated at a high rotation



Figure 20: Spin coater in energy materials lab at USPCASE NUST

The available spin coater at USPCASE NUST is vacuum spin coater VTC-100. A vacuum pump is attached to spin coater. Rotation speed in spin coater VTC-100 varies from 500rpm to 8000rpm.

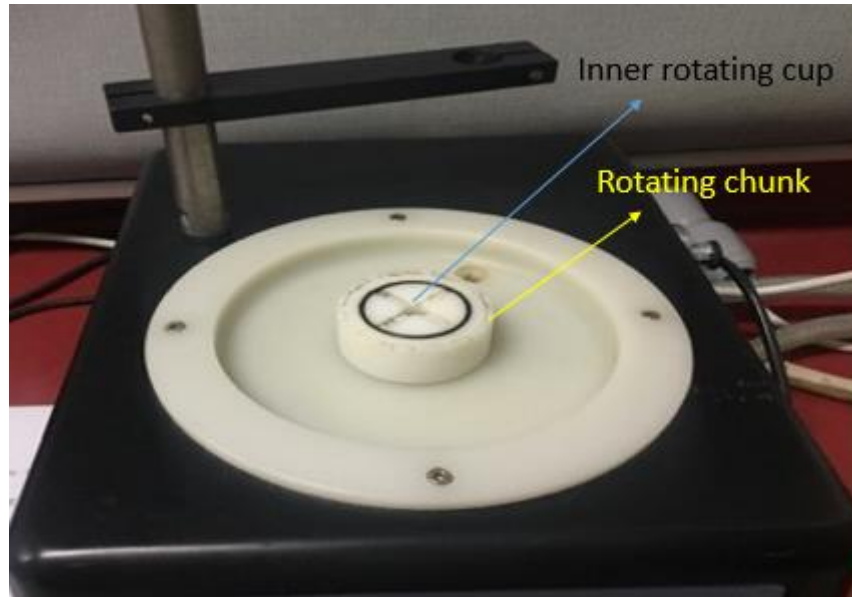


Figure 21: structure of spin coater



Figure 22: vacuum pump attached with spin coater

Spin coater works on the principle of centrifugal force.

The experimental steps involved in the spin coating are the following.

1. First of all, check lubricate level in the vacuum pump.
2. Place a glass or any other substrate on which coating is required on rotating chunk.

3. There are two cups inner cup and outer cup as shown in the Figure. Place the substrate on the center of rotating chunk.
4. Switch on vacuum pump by pressing “pump” button on control panel.
5. Setting for spin coating is done by pressing “FCN” button. By pressing “FCN” button  $t_1$  will start blinking so time for low rpm is set by using + and – sign.
6. After setting time  $t_1$ , press “FCN” and then  $sp_1$  will start blinking. Now set speed in rpm. At  $sp_1$  spin coater will rotate for  $t_1$  time.
7. Similarly set  $t_2$  which is normally higher than  $t_1$ .
8. Set high-speed  $sp_2$ .  $Sp_2$  vary from 1500 rpm to 5000 rpm depending upon viscosity of the solution and required thickness of deposited material.
9. Then press the start button on control panel. Rotating chunk will start rotating at speed  $sp_1$ .
10. Put few drops of prepared solution on the substrate.
11. It will change speed to  $sp_2$  value after time  $t_1$  seconds. For time  $t_2$ , the rotor will rotate at speed  $sp_2$  for  $t_2$  seconds.
12. Rotator will stop automatically after completion of time  $sp_2$  and vacuum will stop about 30sec after stopping of rotating chunk.
13. Take the coated substrate out and clean the equipment properly.

### **3.1.3 Chemical Vapor deposition (CVD) Technique**

Chemical vapor deposition is one of the most important method of thin film fabrication. It is a process in which material is heated and converted to vapors form and then transported via the vapor phase to the reaction chamber. In the reaction chamber it decomposed on a heated target as a result of which chemical reaction happens and thin film is formed.

Many materials are deposited using CVD and related techniques like Metals oxides, sulfides, nitrides, phosphides and silicides. CVD processes are categorized according to Application, Process, Precursor and chemical reaction used. Optoelectronic material grown is one of the most important benefit of using CVD technique.

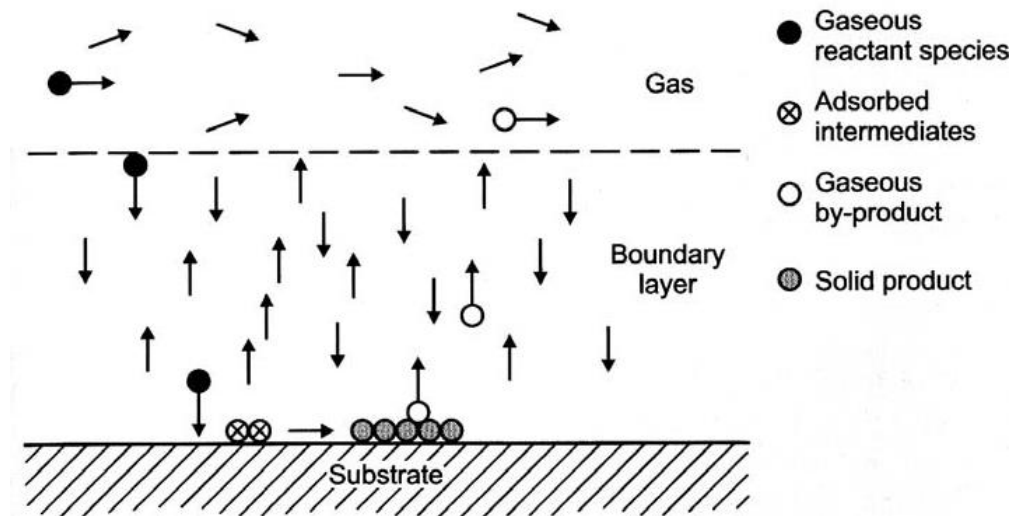


Figure 23: Schematics representation of steps of CVD process [5]

Multiple materials can be deposited on the substrate as well. There are many parameters influencing the growth and properties of the coating. Growth rate depends upon application and for electronics; normally it is around  $0.1 \mu\text{m}/\text{min}$ .

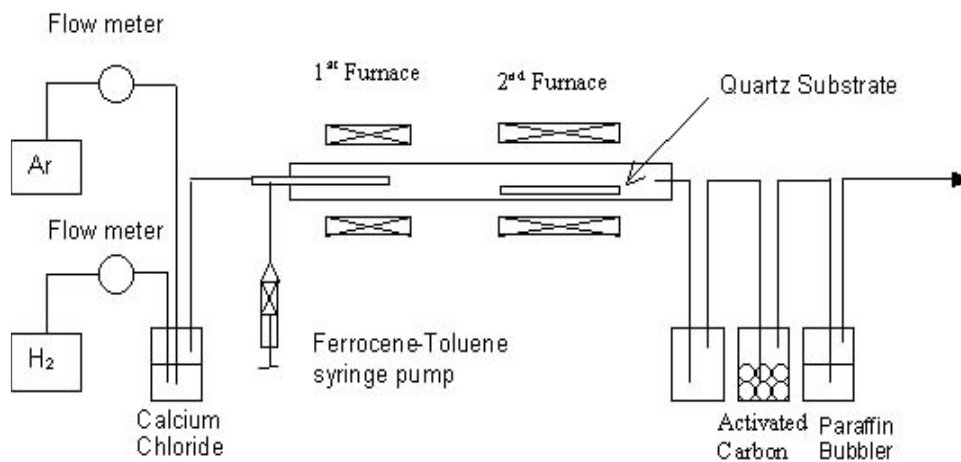


Figure 24: CVD schematic diagram for CNTs activation [7]

The Figure 24 is schematic diagram of activation of carbon nanotube. There are multiple metal composites, which are prepared through chemical vapor deposition technique. NiO-CNTs

composite is one of the most important composite prepared by using CVD method. CH<sub>4</sub>/H<sub>2</sub> corona discharge enhanced CVD method is also one of the method of preparation of NiO-CNTs composite. Catalytic chemical vapor deposition process is also another type of chemical vapor deposition process. In this technique, Catalytic source and carbon are used for purification and functionalization of carbon nanotubes. Camphor, which is industrially available carbon precursor, is used because it is easily available and cost effective. Detail experimentation and NiO-CNTs preparation process is discussed in next chapter.

## **3.2 Characterization techniques**

There are multiple techniques used for characterization of counter electrode and complete solar cell. Scanning electron microscope, X-ray diffraction, Hall Effect equipment and cyclic voltammetry is used for characterization of counter electrode. The solar simulator is used to find the efficiency of the complete DSSC. Thermal gravimetric analysis is used to find the aging effect on solar cell and degradation of a solar cell with time and with temperature.

### **3.2.1 Scanning electron microscope (SEM)**

The scanning electron microscope is used for the surface study of the specimen. It can magnify the sample surface up to 200000 times. SEM is equipped with an electron gun, a condense lens, and an objective lens to produce electronic probe.

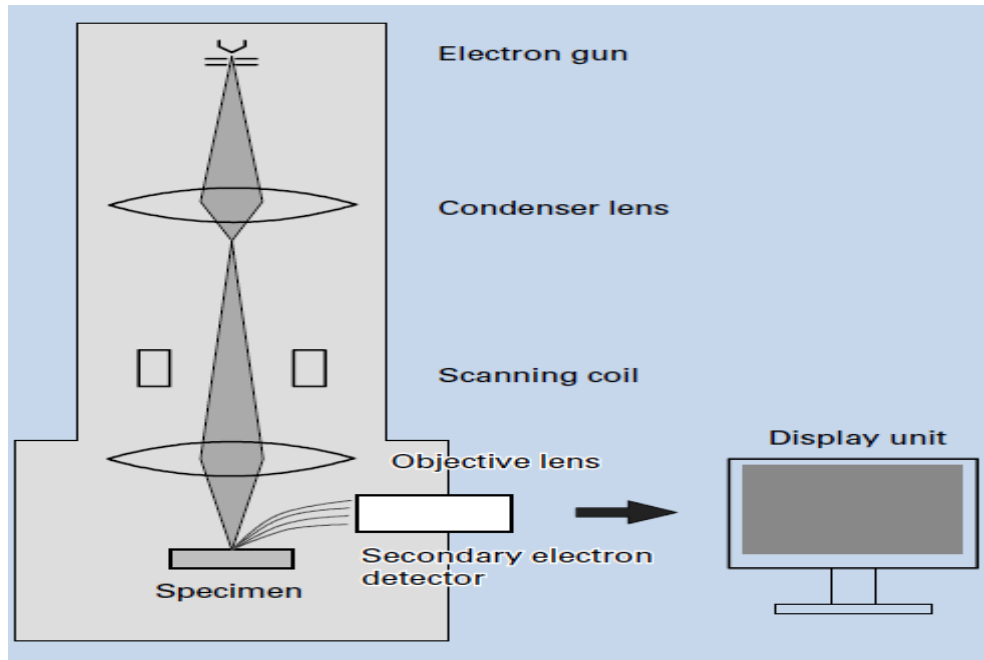


Figure 25: internal structure of scanning electron microscope [9]

SEM is used for topographic analysis while topography property is how a material looks like. Similarly, SEM is also used for Morphology (the shape and size of the particle) analysis of the material. The composition of material which means elements and compounds of the specimen under study can be determined through SEM. Crystallographic information which means how atoms are arranged in the material is derived from SEM results. SEM is preferred over ordinary microscope due to its higher magnification, higher depth of field and high resolution. Through SEM clear images can be obtained at nano meter resolution. Resolution is an ability to study two closely spaced points. Sample needs to be prepared for SEM testing. The sample should be conductive otherwise sample will start sparking and there will be no visible image. The nonconductive sample should be coated with either carbon or gold to make the sample conductive. There are back scattered electrons, beam electron and secondary electron which determine the properties of the specimen. SEM electron “kicks off” the electron from shells of the specimen under testing.

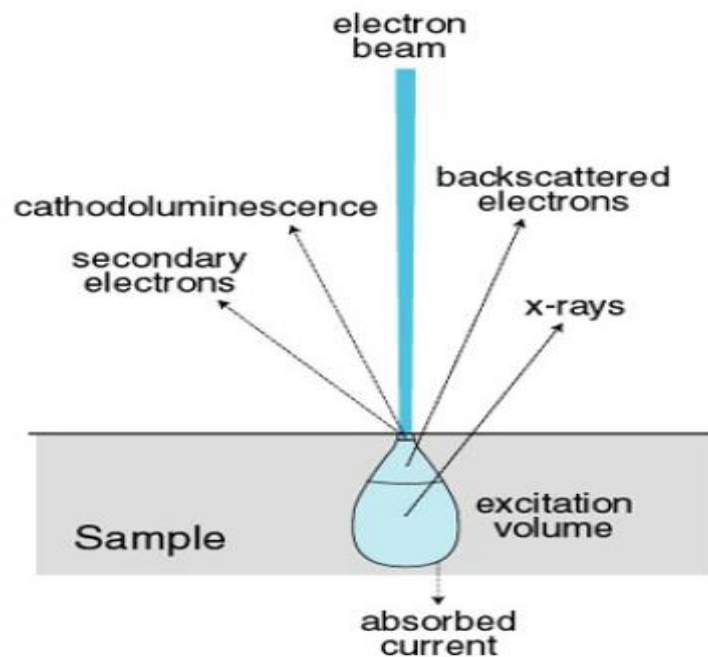


Figure 26: working principle of SEM [5]

The Figure 26 shows that electron beam collides with the sample and then few electrons back scatter and few are a secondary electron. High vacuum is created in the chamber to avoid collision with electron [3] [4] [5].

### 3.2.2 Energy dispersive spectroscopy (EDS)

Energy dispersive spectroscopy is also attached to SEM and through EDS composition of the sample at a particular point is determined. EDS uses X-rays emitted from the sample while the sample is being bombarded with a beam of electrons at a specific point. EDS provides localized chemical composition of the sample. It can identify all elements from atomic number 4 to 92. EDS is not a surface technique [6] [7].

### 3.2.3 X-ray Diffraction (XRD)

XRD works on the principle of Bragg's law. Bragg's law was derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913. XRD is used to measure the average spacing between the layers of the atoms of the specimen. XRD is used to determine crystal structure of materials and determine the orientation of crystal atoms.

Bragg's law is  $n \cdot \lambda = 2d \sin(\theta)$

Where  $d$  is the space between the atoms.

When a beam of X-rays collides with the lattice plane of the structure of the material under testing, every atom of the material emits a secondary wave. These emitted secondary waves then interfere with each other and finally produce a diffracted beam [8] [9].

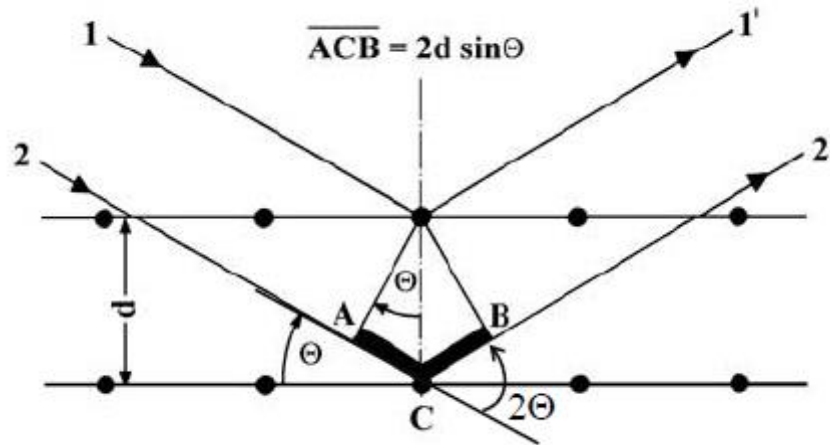


Figure 27: Bragg's law as working principle of XRD [9]

XRD equipment work on the principle of Bragg's law derived from law of conservation of energy and law of conservation of momentum [10] [9].

The distance between the two planes is " $d$ ". When secondary waves interfere constructively it will show a peak on the graph. The sample should be in powdered form for XRD or it should be coated on a substrate as a thin film. XRD is used for phase identification, radial distribution function, crystal distribution function, the percentage of material as crystalline or amorphous and determine the crystal structure of the sample [11] [12] [13] [14].





Figure 28: XRD machine (D-8 Advance) available at USPCASE

There are two arms like structure in XRD machine. X-rays source is on one side while the detector is on another side of the machine. We can scan the sample from  $0^{\circ}$ - $90^{\circ}$  but to be on the safe side we restrict from  $10^{\circ}$  to  $80^{\circ}$  [15].

### 3.2.4 Hall Effect

Hall Effect is an equipment, which is used to find the resistance, resistivity of film deposited on the substrate and charge mobility. Hall Effect equipment works on the principle of Lorentz force. Electricity and magnetic forces are used in Hall Effect equipment. As the magnetic field is increased, the electrons are deflected accordingly; the higher the current, the more electrons there are to deflect. Hall-effect probes are sophisticated and expensive needle like structure which connect to the surface of the film and current flow between these probes. Hall Effect sensors detect the current and give the value of resistance, resistivity, charge carrier concentration and mobility.

Hall Effect measurement system is used to find voltage difference between both diagonal sides of the probes, when current is flowing and magnet field strength is being applied, in perpendicular to flowing current direction. The Hall Effect measurement system is used to find the resistivity,

concentration, and mobility of semiconductor (P type and N type). The software used in the solar simulator is I-V curve capability to check ohmic properties of the semiconductors and conductive coatings. The output of Hall Effect is resistance and curve between voltage and current. Hall effect measurement can be done at 77 K and 300 K (room temperature). Hall Effect measurement's theoretical basis is Lorentz Force and Van der Pauw technique.

Permanent magnets and an integrated circuit switching system are used instead of heavy electromagnets and separate constant current source and DVM.



Figure 29: hall Effect measurement equipment at USPCASE NUST

The coated sample is cut according to the size of the four probes mounting board. The sample is placed at “+” size of the mounting board and probes are attached to the corner of the sample.



Figure 30: Sample-mounting board

Four sample mounting board is attached to the sample holder. Magnetic kit has two poles north (N) and south (S) pole. When the test is started, first north (N) to south(S) pole is applied and then poles are reversed from south (S) to north (N). Output graphs are temperature Vs concentration, temperature Vs mobility, temperature vs resistivity and IV curve. Temperature is varied from room temperature to 773 K.



Figure 31: Sample kit with 0.55 Tesla magnet supplied standard with the system

These obtained graphs give us the complete detail of the sample especially resistance of the material. In this project, the main requirement is to increase the conductivity of the thin film.

### 3.2.5 Cyclic Voltammetry (CV)

Voltammetry is a branch of experimental chemistry, in this experiment potential applied at working electrode and resulting current is measured, as a function of potential. Cyclic voltammetry is a technique used for analysis of current and voltage behavior in an electrochemical reaction. In CV, voltage is changed at a constant rate between two limits and change in current is monitored accordingly in an electrochemical cell. CV is most powerful tool to characterize the electrochemical behavior of analyses that can be electrochemically oxidized or reduced. The voltage is determined according to Nernst equation. The concentration is varied according to Fick's first law and state the mass transfer from high concentration to low concentration[16].

$$i_p = (2.69 \times 10^5) n^{3/2} S D_A^{1/2} v^{1/2} C_A,$$
$$\frac{\partial}{\partial t} (C_A) = D_A \frac{\partial^2}{\partial x^2} (C_A)$$

$D_A$  is diffusion coefficient of reactants.

The current is varied according to the equation given above.

$n$  = No of electrons being gained in the reduction of the electrochemical reaction

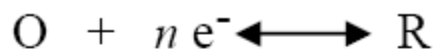
$S$  = Area of the working electrode in  $\text{cm}^2$

$D_A$  = the diffusion coefficient

$v$  = sweep rate

$C_A$  = Bulk molar concentration

This fundamental expression simply specifies the relationship between the potential of an electrode and the concentrations of the two species (designated O and R) involved in the redox reaction at that electrode:



$$E = E^{0'} + \frac{RT}{nF} \ln \left( \frac{C_O}{C_R} \right)$$

$E^{0'}$  is the redox potential for the couple involving O and R and  $C_O$  is the concentration of the oxidation and  $C_R$  is the concentration of the reduction half. Ratio of  $C_O$  and  $C_R$  is very in cyclic voltammetry. If the concentration at the electrode and in the solution is same that means, there is no driving force from solution to the surface of the electrode. The driving force of analyte from solution and electrode is due to diffusion [17]. The concentration difference in the solution and near electrode or at the electrode determine the voltage according to the Nernst equation.

There are following components of CV results

- Electrodes
  - Working electrode
  - Reference electrode
  - Counter electrode
- Solvent
- Computer operated software
- Supporting electrolyte (Sodium sulphite).

Applied voltage is kept between 0.8 V and -0.8 V as solution is aqueous and it above 1V aqueous solution start splitting.

There are following types of currents and voltages involved in CV.

- Peak cathodic current  $i_{pc}$  is current flows when rate of reduction is maximum.

- Peak anodic current  $i_{pa}$  is current flows when rate of oxidation is maximum.
- Peak cathodic voltage  $E_{pc}$  is potential at which rate of reduction is maximum.
- Peak anodic voltage  $E_{pa}$  is potential at which rate of oxidation is maximum.

There are following types of electrodes involved in CV analysis.

- Working electrode is the electrode on which potential is varied with time where redox reaction of analyte occur.
- Reference electrode is the electrode with respect to which the potential of working electrode is made e.g (Ag/AgCl electrode).
- Reference electrode is the electrode as it completes the circuit by conducting e- through solution to the working electrode.
- Supporting electrode is nonreactive electrolyte to conduct current.

### **3.3 Assembling of complete DSSC**

The deposited counter electrode is tested by fabricating complete solar cell using the microfluidic technique. The microfluidic sealing technique is to join photo anode and counter electrode separated through the spacer. An electrolyte is filled in the space created due to the spacer. Two holes are drilled in counter electrode (coated PET) so that electrolytes could be filled between photo anode and the counter electrode.

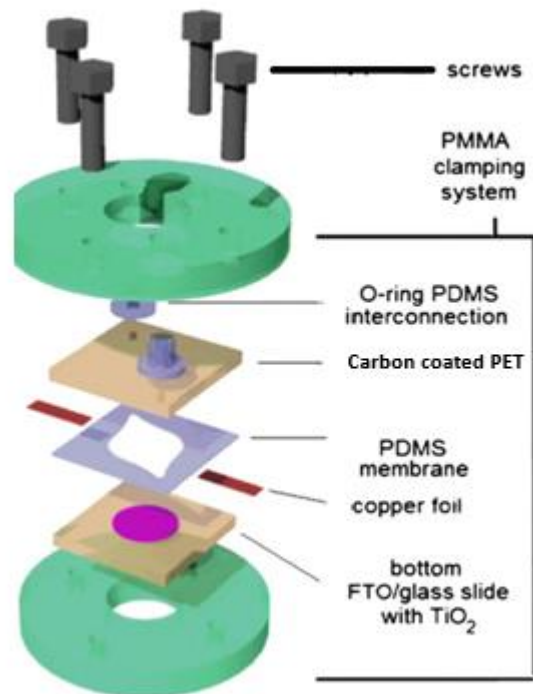


Figure 32: Complete assembly of DSSC using microfluidic technique [15]

A standard photo anode is a metal oxide layer deposited on an ITO/FTO coated conductive glass. A dye solution is being prepared by dissolving dye in absolute ethanol. This solution is sonicated for half an hour to ensure proper dispersion of the dye in ethanol. The metal oxide based photoanode is dipped in the dye solution for 2-3 hours and then cleaned with distilled water. In DSSC assembly “Iodolyte AN-150, Solaronix” is used as electrolyte. The counter electrode is also cleaned with ethanol before microfluidic sealing. PDMS membrane is used as a spacer between photo anode and counter electrode. A cell is being assembled according to the Figure above. Copper foils are used to connect the terminals for testing.

### 3.3.1 Characterization of DSSC

The solar cells are tested under one sun and air mass (AM-1.5). solar cell is characherized in IV measurement system at Air Mass(AM) 1.5. To simmluate the solar spectrum accuraatly, high pressure xenon arc lamp sources and air mass . filters are used. The IV profiler is an equipment used for solar cell characterization. Efficiency is measured through IV measurement system. A

graph is obtained between the output voltage and output current when solar simulator light is applied through series arc lamp. The intensity of solar light on earth is about  $100 \text{ mW/cm}^2$ . The graph obtained through solar simulator is called IV curve.

A solar simulator consists of main two components

1. Xenon Arc Lamps as light source.
2. Optics and filters required to get the output according to test requirements [1].

Xenon lamps are used because spectrum of xenon is very close to sun light so xenon light can better simulate sun light.

There are few steps involved in solar simulator characterization.

1. Switch on the setup and make sure that all fans are working properly.
2. Turn ON the lamp and wait for until it stabilize.
3. One the lamp shutter. It is necessary to wear safety gloves for safety purpose.
4. Calibrate the setup by using standard calibration solar cell provided by the manufacturer.
5. Connect the cell (required to test) instead of standard calibration cell.
6. Connections should be proper otherwise, our results will not be correct.

There are four important values to be confirmed of standard solar cell, which are over circuit voltage, short circuit current, fill factor and efficiency of the solar cell. Values of these parameters are being provided by the manufacturer.



The light source is monochromatic and output of the light source is equivalent to one sun. Arc lamp and mercury xenon lamp both are used in the solar simulator. The solar simulator used in this project is manufactured by Scienectech. Arc lamp used in equipment is Scienectech arc lamp system is 201 series lamp and power supply used is 501-300 series.

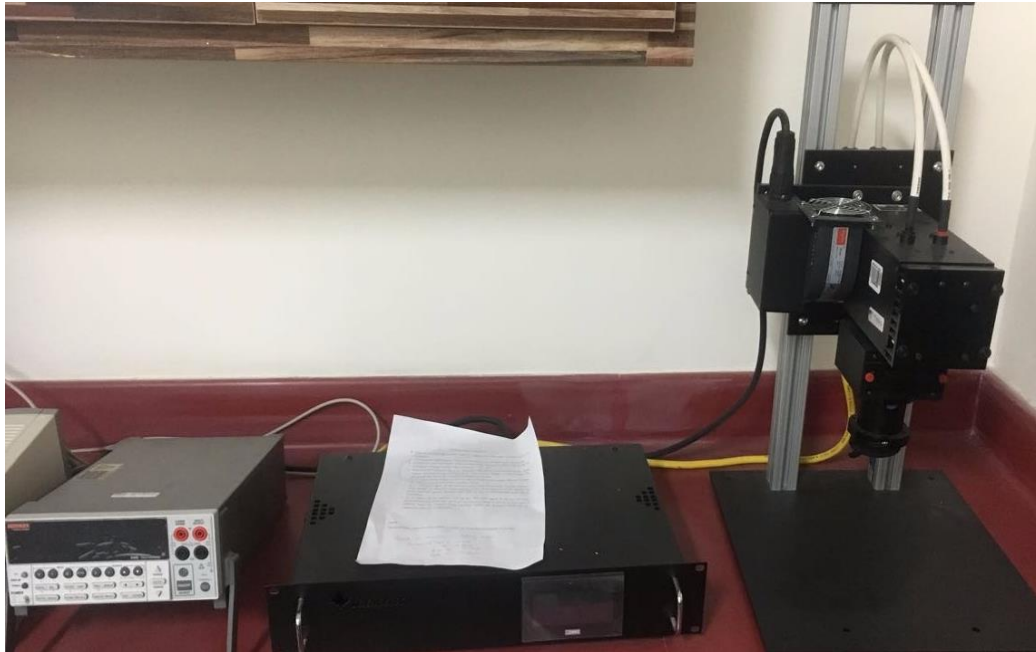


Figure 33: Solar simulator in advance energy materials lab at USPCASE NUST

Software used in the solar simulator is “SciRun”. In software, there is multiple sweep setting which are a normal sweep, reverse sweep, dual sweep, and dark sweep.

In the normal sweep, sweep load voltage from 0V (short circuit current) to Voc (open circuit voltage).

In reverse sweep allow the user to specify from IV sweep from open circuit voltage (Voc) to short circuit current (Isc) instead of normally operating condition Isc to Voc.

In dual sweep, the bidirectional sweep is performed to examine hysteresis effects.

In dark sweep current limited reverse voltage sweep from 0 to -10 volts under the dark condition to find the shunt resistance and effect of breakages in the solar cell.

Through solar simulator, output of concentrated solar cell can also be calculated. The concentration of up to 100 suns can be achieved through xenon lamp and an arc lamp.

In IV measurement system, the output is  $V_{oc}$ ,  $I_{sc}$ , fill factor (FF) and efficiency. Fill factor is term explaining the ideal behavior of the solar cell.

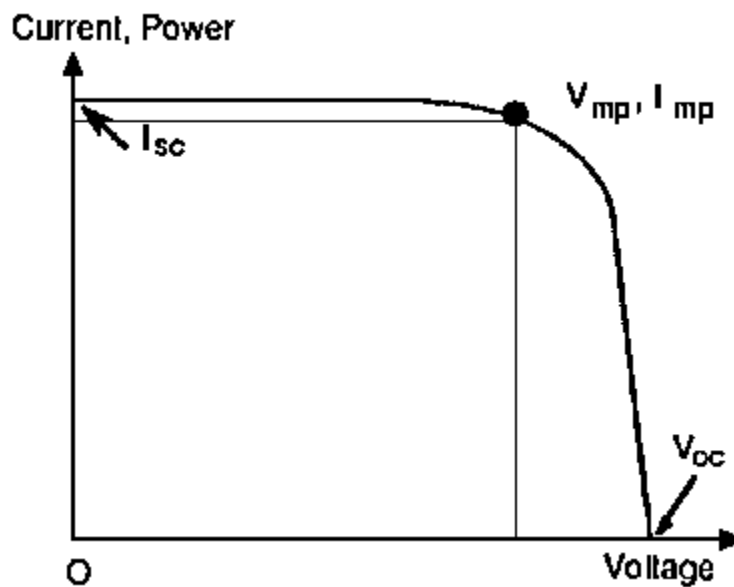


Figure 34: output curve of IV measurement of solar cell at AM 1.5

The IV measurements are also taken in the dark as well so better characterize a solar cell. The IV measurement at AM 1.5 is like solar cell working in the environment outside. By using IV measurement, a solar cell can be categorized based on fill factor, efficiency,  $V_{oc}$  and  $I_{sc}$  of the solar cells.

## **Chapter summary**

In this chapter, experimental techniques and characterization techniques are being discussed. Counter electrode of DSSC is fabricated by using spin coating technique, electrospinning technique and doctor blade technique. Two techniques spin coating and electrospinning techniques are used in experiments and both techniques are discussed in detail in this chapter. In electrospinning and spin coating techniques, solution preparation for deposition is very important because deposition depend on multiple factors and solution preparation is one the most important factor. Equipment working process and experimental procedures of electrospinning and spin coating techniques are discussed in detail. After this, characterization techniques are discussed in detail. Morphology of material is being find using X-rays diffraction (XRD) technique. Similarly to find the structural details of the material, scanning electron microscope (SEM) analysis technique is also being performed. Hall Effect technique is used to find the conductivity of the deposited films. Similarly, cyclic voltammetry is discussed in this chapter. CV is used to find the catalytic activity of the counter electrode. Detail and working principle of both techniques are discussed in detail. Dye sensitized solar cell is fabricated using microfluidic analysis. Then complete cell is tested under IV profiler at AM 1.5.

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# Chapter 4: Experiments

Counter electrodes for DSSCs are fabricated by using different materials and fabrication techniques. These techniques and materials are discussed in detail in this chapter.

## 4.1 Materials

Multiple polymers are being used for dispersion of carbon nanotubes. Polyvinyl pyrrolidone and poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) are polymers used for dispersion of carbon nanotubes. Dimethyl sulfoxide Fisher Bio Reagent of 99.8% with boiling point 189°C is also used in experimentation.

All chemical and precursors like Ethanol (99.9%), Ethylene Glycol, Nickel acetate, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> are purchased from Sigma.

## 4.2 Growth of Nanomaterials

The nanomaterials are prepared by using chemical vapor deposition (CVD) and co-precipitation method.

### 4.2.1 Growth of carbon nanotubes

Multi walled carbon nanotubes (MWCNTs) are prepared through catalytic chemical vapor deposition (CVD) process, which has already been reported ELSEVIER [1] and described here briefly. Catalytic source (iron) and carbon (camphor) are used for growth of carbon nanotubes. Camphor which is industrially available carbon precursor is used because it is easily available and cost effective [1][2].

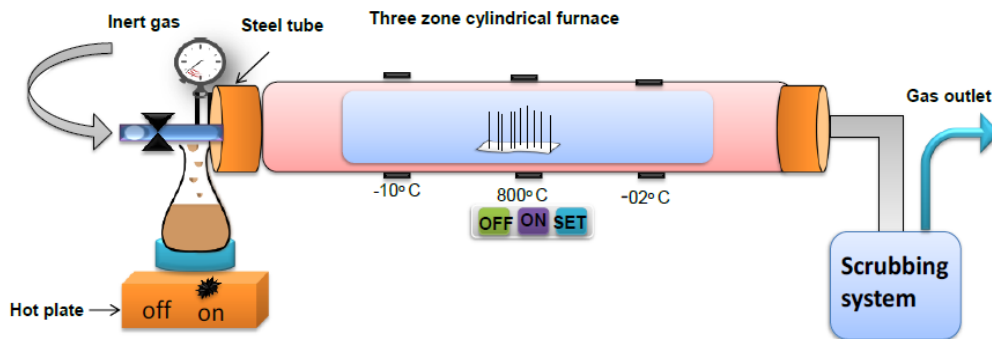


Figure 35: CVD setup for preparation of CNTs

The setup consists of three zones cylindrical furnace. Nitrogen is used in this setup to keep the setup inert. In flask, assembly is placed on a hot plate and furnace temperature is kept at 850°C. Reagent will start vaporizing after attaining 200°C. Vapors will flow due to the proper temperature difference. Carbon species and iron constituents are delivered through high-temperature furnace due to the pyrolysis. Thus carbon nanotubes were grown by the deposition of carbon species on Si substrate and iron particles acted as a catalyst. MWCNTs are purified through a thermal treatment, in which CNTs are heated at 450°C for 4 hours. Sulphuric acid and nitric acid are mixed in 3:1 and functionalized it at environmental temperature. PH of CNTs is made normal by washing the sample with ionized water. Washing is done until PH of the sample is neutralized. CNTs are dried at 100°C [3] [4].



Figure 36: Flow diagram of preparation of functionalized CNTs

These prepared CNTs were purified by thermal treatment and functionalized using chemical process.

Functionalization is basically a process of improving the surface properties of CNTs. There are two types of types of functionalization, chemical and physical functionalization basis on the interaction of CNTs and active materials. In this case, functionalization is of CNTs is performed to increase its interaction with NiO to form better composite material.

Chemical functionalization is basically based on covalent bond of functional groups onto carbon forms of CNTs. Defects can be formed at the end cap of the carbon nanotube or at the side wall. To perform this process there is need of high reactive materials. The process used here is chemical process of functionalization of CNTs. In this process, covalent functionalization caused variation in hybridization of CNTs is varied from  $sp^2$  to  $sp^3$  [6]. There is also another method called defect functionalization of CNTs and this done by using strong acids. These strong acids cause oxidative damage to the CNTs framework and this leave a hole functionalized with oxygenated functional group. The strong used are normally  $HNO_3$ ,  $H_2SO_4$  or a mixture of these both in different ratios. These cause defects at the end sites of the tubes [7]. These defects can attract multiple groups thus this process is very useful to increase the conductive properties of CNTs. Due to functionalization, CNTs become soluble in multiple organic solvents because CNTs can possess polar as well as non-polar groups. Thus modification of CNTs improve compatibility and solubility [8][9].

#### **4.2.2 Growth and preparation of NiO and NiO-CNTs composite by co-precipitation method**

NiO-CNTs nanocomposite is prepared by using co-precipitation method. In co-precipitation method for the preparation of NiO, EG solution is prepared by dissolving 0.5g of EG of in 100ml of distilled water and heated at  $80^\circ C$  for 1 hour. A 25 ml solution of nickel acetate is prepared by dissolving 0.5g of nickel acetate in dis- $H_2O$ . NiO solutions is mixed and poured in EG solution and then stirred for around 1 hour. 0.1M NaOH solution is added dropwise to flask containing both EG and nickel acetate solution. When PH=12 is attained then put the solution for stirring for 3 hrs. The precipitates are filtered and washed multiple times with distilled water to neutralize the PH of the precipitate. After this, precipitates is dried at  $100^\circ C$  and calcination is performed for 4hrs at  $350^\circ C$ [1][2][5].

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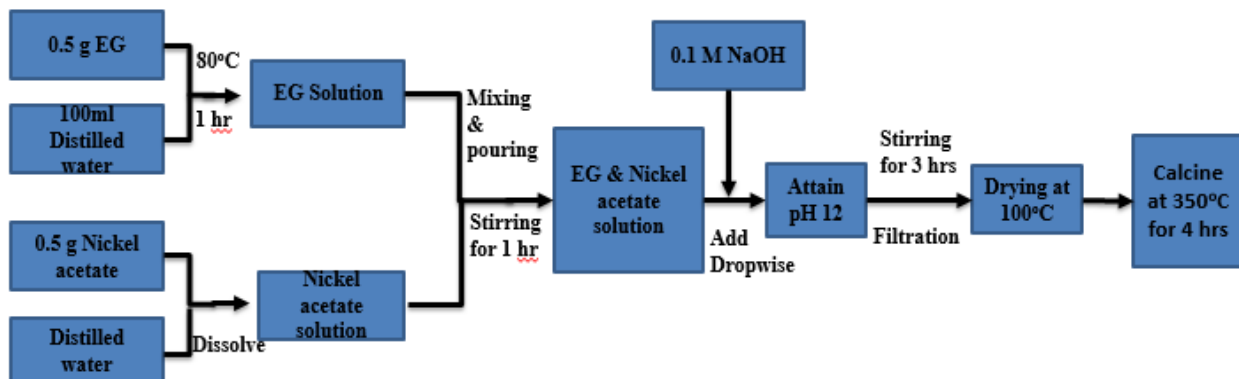


Figure 37: Flow diagram of preparation of NiO nanocomposite

NiO-CNT composite is highly conductive material and used for preparation of electrode for batteries, capacitors and solar cells. NiO-CNTs composites is prepared in lab with different ratios of NiO and CNTs and finally an optimized ratio is achieved. Co precipitation method is being used for preparation of NiO-CNTs composite as well. NiO-CNTs composites are prepared by mixing NiO and MWCNTs. 0.2g of EG is dispersed in deionized water and heated for 1 hour.

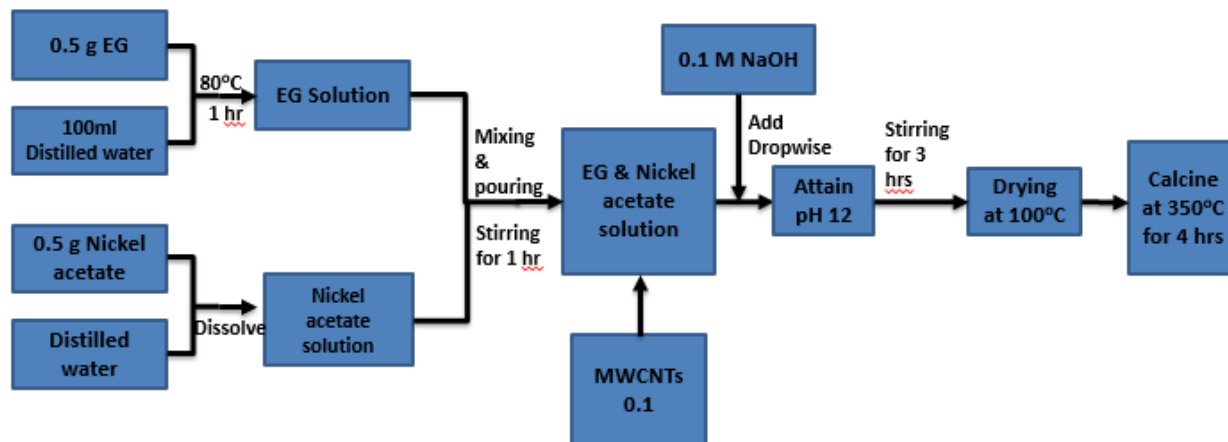


Figure 38: Process flow diagram for preparation of NiO-CNTs

### 4.3 Solution preparation for electrode deposition

Poly vinyl propodilene (PVP) is a polymer which is being used to fabricate NiO/CNTs/ NiO-CNTs based counter electrode for dye sensitized solar cells. 5mg of MWCNTs are dispersed in 5ml of dimethyl sulfoxide. This solution is sonicated for 1 hour and then stirred for 48 hours. 0.5ml of PEDOT: PSS is added to MWCNTs solution. [10].

1 gram of polyvinyl pyrrolidone is mixed in the already prepared PEDOT: PSS NiO-CNTs solution. This solution is kept for stirring for 12 hours then sonicated for one hour. In this process, it is also necessary to observe the viscosity of the solution and if required increase sonication or stirring time. To control the viscosity properly, add a small amount of Polyvinyl pyrrolidone step by step.

Table 2: Solution composition

Solution	PVP(mg)	PEDOT:PSS(ml)	DMSO(ml)	CNTs(mg)	NiO(mg)	NiO-CNTs
Solution 1	100	3	20	10	-----	-----
Solution 2	100	3	20	-----	20	-----
Solution 3	100	3	20	-----	-----	10

#### 4.4 Fabrication of counter electrode by spin coating

The ITO coated PET and FTO glass are deposited by using spin coating technique. This technique is used by varying the prepared solution and multiple factors in deposition technique.

Nano materials are dispersed in PEDOT:PSS and then coated on ITO coated PET (purchased from sigma Aldrich) and FTO (purchased from sigma Aldrich) glass. Spin coating technique is used for coating the PET and FTO glass. Multiple coatings are required for fabrication of counter electrode because a single coating is not enough to get fruitful results. Ito coated PET piece of 2cm \* 2cm are coated because available Photoanode is of similar size. The sample is not highly viscous so we keep the rotation speed low so that highest thickness could be obtained. The primary rotation speed is 500 rpm and secondary speed is 1000 rpm. The time t1 is set as 15 sec and similarly time t2 is set as 20 sec. The coated PET and glass are dried in drying oven at 60°C for 90 mints. The obtained sample are then tested under hall effect equipment to find conductivity of the deposited film and to find charge carrier mobility [11][12].

#### 4.5 Assembling of complete Dye sensitized solar cell

The microfluidic technique is used to connect all the components of dye sensitized solar cells. This complete cell is then further tested under solar simulator and IV curve is being obtained as results. ZnO is deposited on FTO conductive glass following the method described in published article [2]. Photoanode is placed on the hot plate at 70°C for 10 mints and then dipped in a dye solution for 6 hours. After 6 hours of dipping, photoanode is taken out of solution and dye is removed carefully with ethanol. The spacer is used to create space for filling of electrolyte between photoanode and the counter electrode [13][14]. After placing the spacer on photoanode, the counter

electrode is placed on top of spacer carefully because both holes of the counter electrode should be within space by the spacer. PMMA clamping is then placed at top of it. Placing of clamping is also very important because we have to fill the electrolyte through the holes of the PMMA clamping. Screws are then tightened with screw carefully. All screws are tightened step by step so that there is no high pressure on any side of the FTO glass [15]. Uneven tightening of the screws can cause breakage of FTO glass. After completing the assembly, the electrolyte is filled through holes with special syringe and a thin plastic tube. “Iodolyte AN-150, Solaronix” is used as an electrolyte in DSSC assembly

## **Chapter summary**

In this chapter, experiments are performed to prepare NiO, CNTs and NiO-CNTs composite. Carbon nanotubes are purified using catalytic chemical vapor deposition. PEDOT:PSS, PVP and PVA are polymers used for polymerization of CNTs. The polymers are used in different ratio to adjust the viscosity of the solution. NiO nano-material is prepared and similarly CNTs are purified. Then using both NiO and CNTs NiO-CNTs composite is prepared. Then solution of NiO, CNTs and NiO-CNTs are prepared. Dye is absorbed on ITO coated PET so form the counter electrode. These solutions are deposited using electrospinning and spin coating technique. ZnO photoanode is used and similarly electrolyte is filled in between photoanode and counter electrode. Complete DSSC is fabricated by using microfluidic analysis. Complete cell is fabricated.

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# Chapter 5: Results and Discussions

Structural, morphological and composition analysis of materials and deposited films are performed by using SEM, EDS and XRD. Electrochemical properties of materials are obtained through cyclic voltammetry while electrical properties are found through Hall Effect.

## 5.1 Morphological, compositional and structural analysis

There are multiple techniques used to find the composition of materials. In morphology and composition analysis techniques, there are SEM, EDS and XRD analysis technique. These techniques inform about composition of the materials and morphology of the material.

### 5.1.1 SEM, EDS and XRD analysis of CNTs

This image clearly shows the formation of CNTs and hence it has been verified that CNTs have been formed properly.

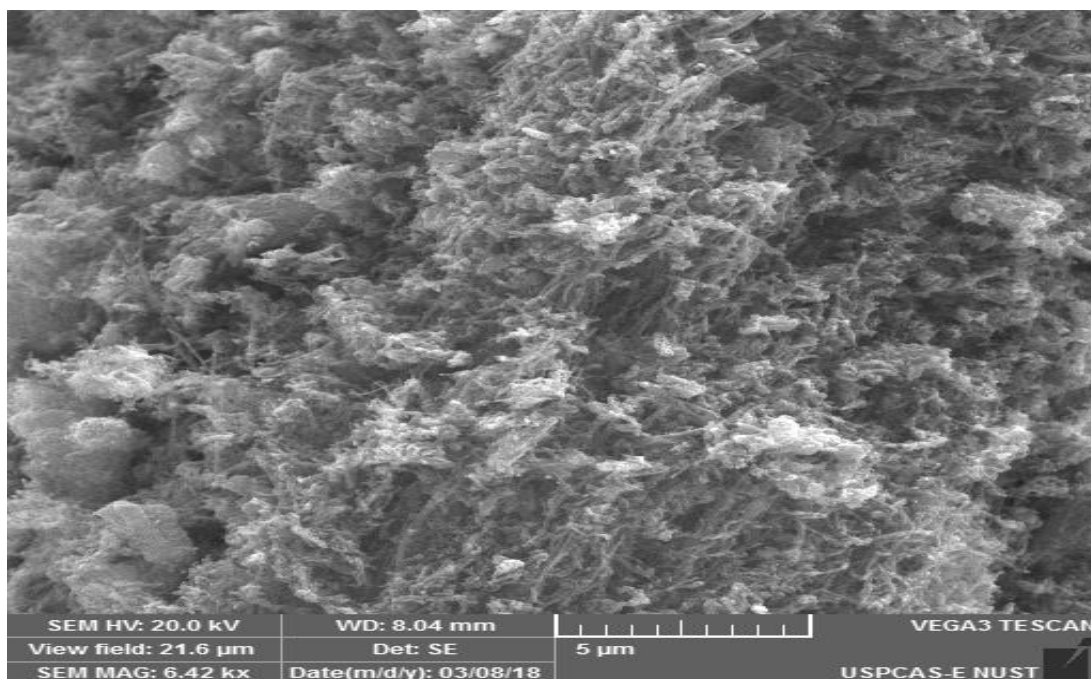


Figure 39: CNTs at 5μm resolution



The Figure 39 shows the SEM images are at 5 $\mu$ m. These clearly show the formation of CNTs. When further go down then it became clearer.

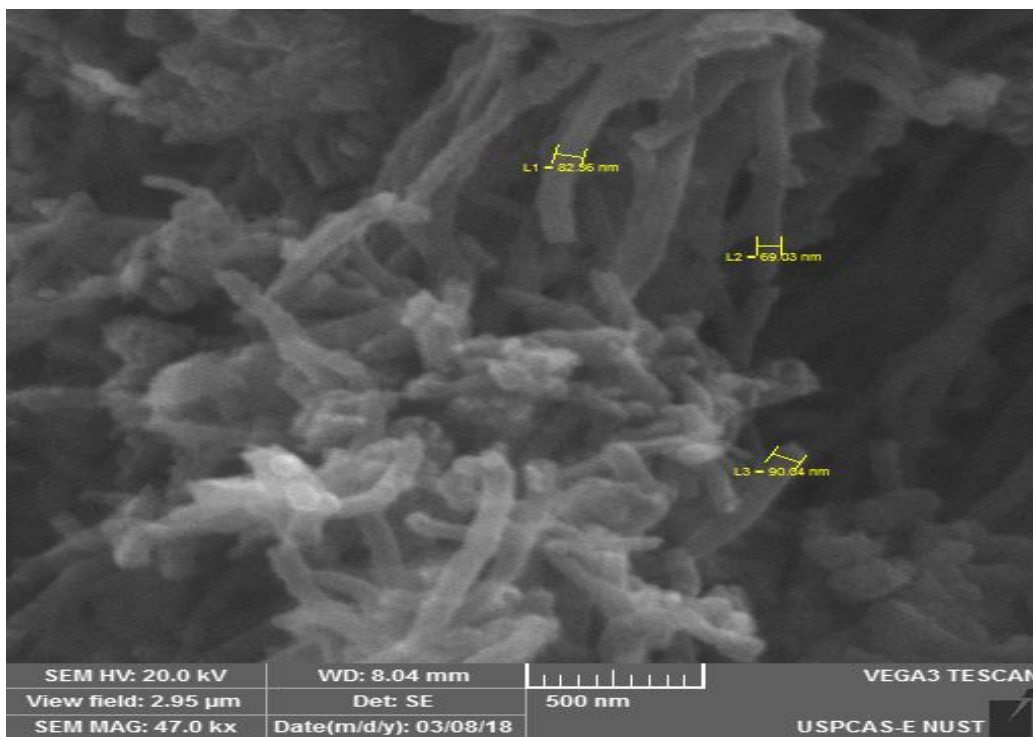


Figure 40: Mapping of CNTs on SEM image at high resolution

The Figure 40 shows the structure of CNTs. The diameter of CNTs is less than 100 nm which are very perfect for fabrication of counter electrode for dye sensitized solar cells. Carbon nanotubes are of very low diameter due to which resistance is reduced. The resistance of the material is inversely proportional to the area of the material so when the diameter of the tube is reduced resistance has increased.

The EDS analysis of the samples show the percentages of the elements in that material. The EDS results of the CNTs are given below.

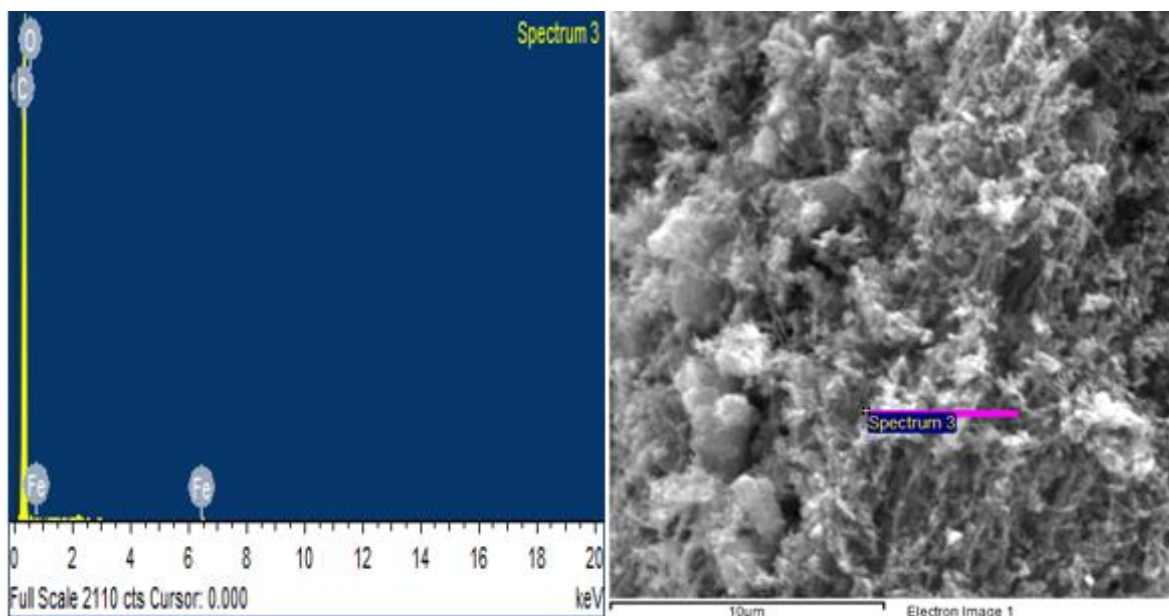


Figure 41: EDS results of the CNTs

The line scan is taken to show the elements present in the sample by taking analysis of a line. The percentage of the elements are given below.

Table 3: Percentage of elements in CNTs

Element	Weight%	Atomic%
C K	94.74	96.26
O K	4.77	3.64
Fe K	0.49	0.11
Totals	100.00	

The above table clearly shows the percentage of the elements in CNTs. Carbon is the major elements in material. Oxygen and iron are impurities. Oxygen is result of heating the material at high temperature due to which oxygen is formed.

This image shows the formation of carbon material. Iron has peaked at that specific point but elemental analysis shows the proper formation of carbon materials.

XRD analysis of CNTs is also performed. The result of XRD result is matched to CNTs [5].

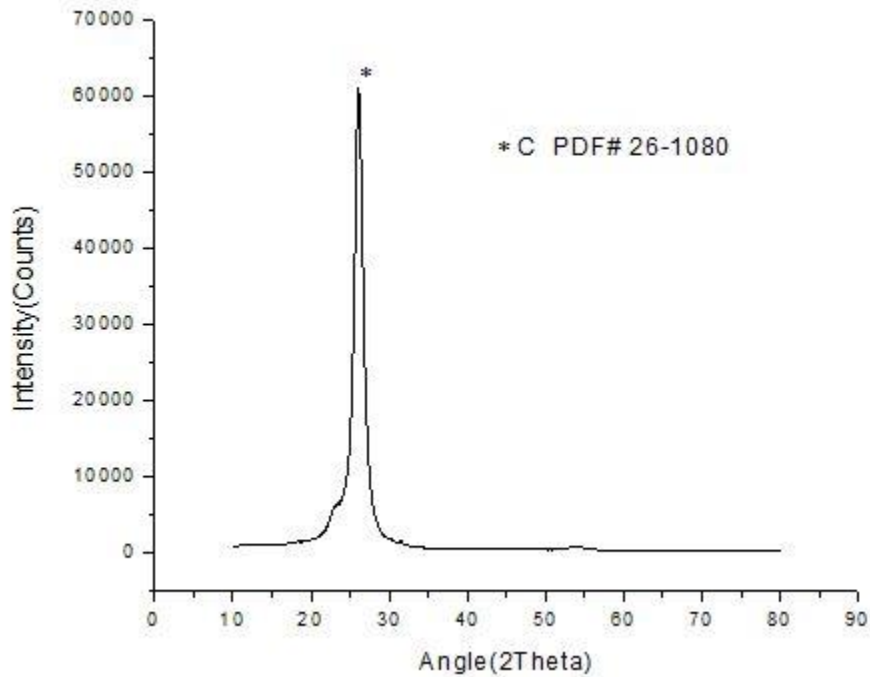


Figure 42: XRD analysis of CNTs

The peak at angle  $26^\circ$  matched the (2 0 0) plane of the carbon which is carbon nanotube. Another shoulder like peak has been observed at 24 which might be due to minute quantity of oxygen and iron.

### 5.1.2 SEM, EDS and XRD analysis of NiO

The images below is SEM image of NiO Nano particles. This image show the structure of NiO. It show diameter of the nano particles.

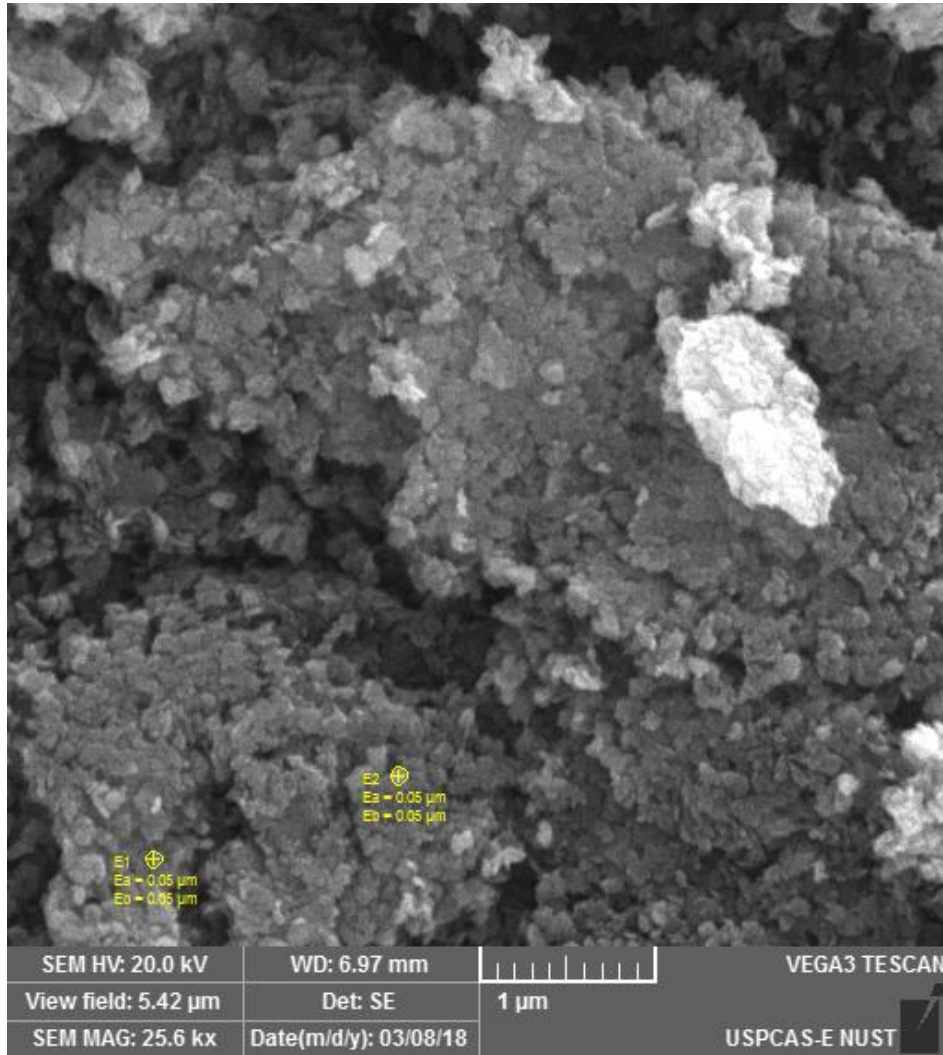


Figure 43: Mapping of NiO on SEM image at 1μm resolution

The image of NiO at 1μm resolution show the Nano structure of NiO. There are particles of 50 nm diameter. These structure are mostly round shape and a few are elliptical as shown in Figure. The image gets a bit unclear at this high resolution.

The EDS result shows the presence of all the elements in that sample. Results of EDS analysis of NiO are given below.

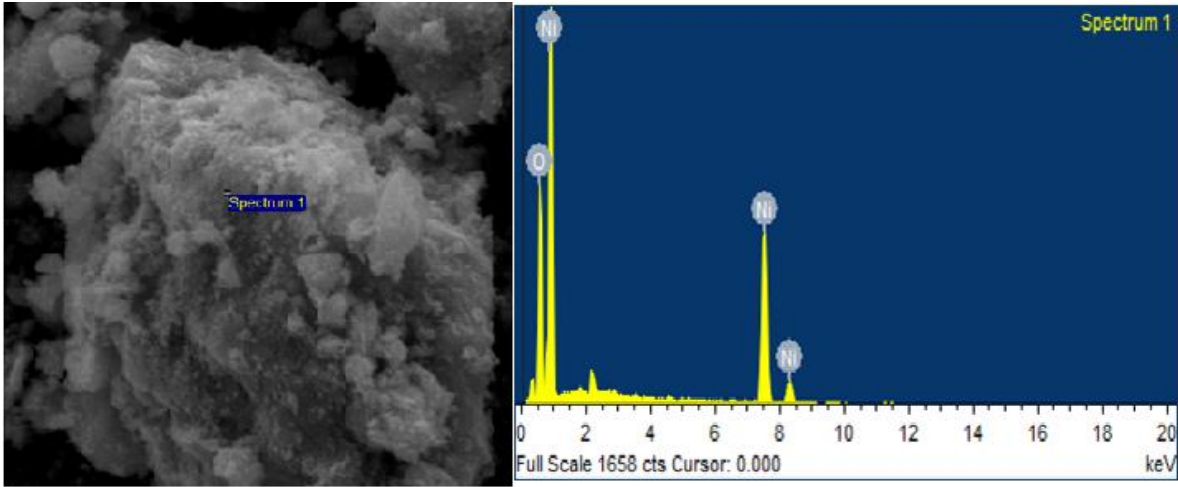


Figure 44: EDS analysis of NiO

The Figure 44 shows the peaks of Ni and oxygen. The percentage weightage table is also given below.

Table 4: percentage composition of NiO

Element	Weight%	Atomic%
O K	45.20	75.16
Ni K	54.80	24.84
Totals	100.00	

The weight percentage composition of Ni is 55 and oxygen is 45. This result is point analysis of NiO. Similar results are being obtained for line analysis of NiO.

XRD analysis of the material is also performed to find the structure and obtained output is the following.

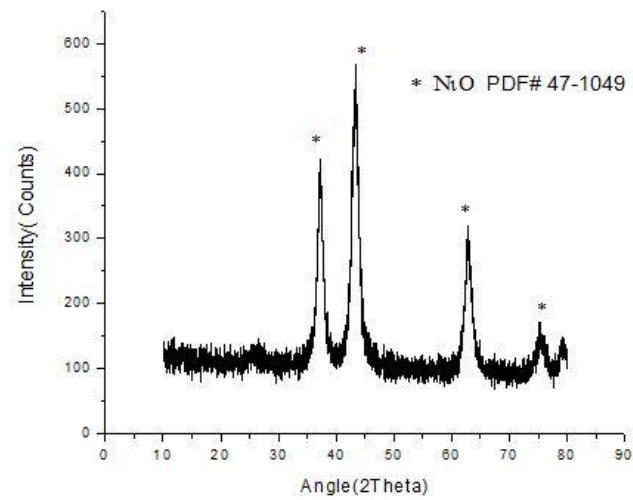


Figure 45: XRD analysis of NiO

The result in Figure 45 is match of NiO [3]. The peak at angle  $36^{\circ}$  (2 theta) is (1 1 1) plane of NiO. The peak at angle  $43^{\circ}$  is of plane (2 0 0). The plane at angle  $63^{\circ}$  is (2 0 0).

### 5.1.3 SEM, EDS and XRD analysis of NiO-CNTs:

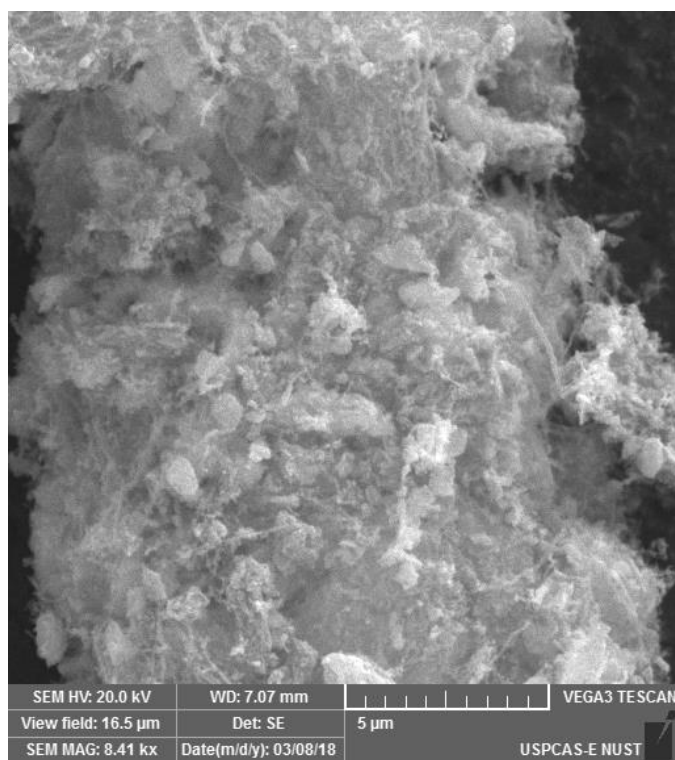


Figure 46: SEM image of NiO-CNTs at 5 um

NiO-CNTs composite are also characterized for morphology, elemental and composition and results are reported in Figure 46, Figure 47, Figure 48 and Figure 49.

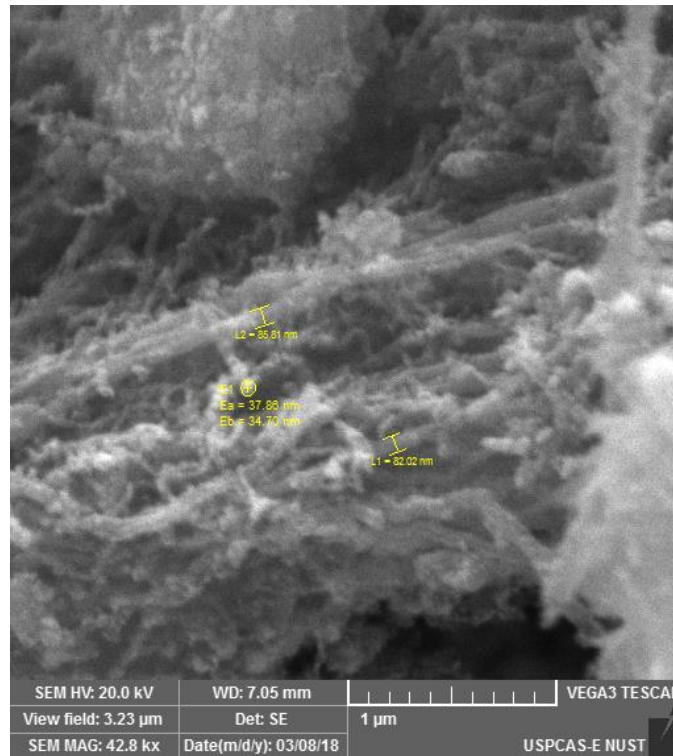


Figure 47: Mapping of NiO-CNTs on SEM image at 1um resolution

As these images at different resolution, clearly shows the formation of CNTs-NiO composite. Diameter of carbon nanotubes is in range of 50 nm to 100 nm. EDS analysis of NiO-CNTs composite is the also given below.



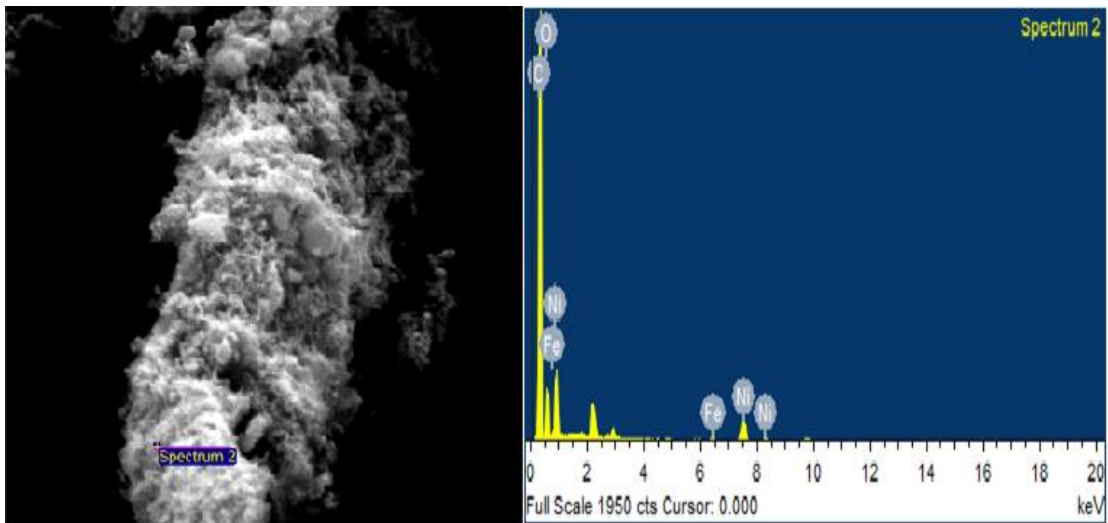


Figure 48: Line EDS analysis of NiO-CNTs

Table 5: EDS results of NiO-CNTs

Element	Weight%	Atomic%
C K	74.68	81.40
O K	21.76	17.81
Fe K	0.09	0.02
Ni K	3.47	0.77
Totals	100.00	

The table 6 shows the percentage of carbon, oxygen and Nickel. Iron is an impurity, which is in very less percentage around 0.21%. The SEM images and EDS results shows the successful formation of NiO-CNTs composite.

XRD analysis of NiO-CNTs is also performed. The result matches the Figure of NiO-CNTs as described in literature. The matched output of XRD is given below.

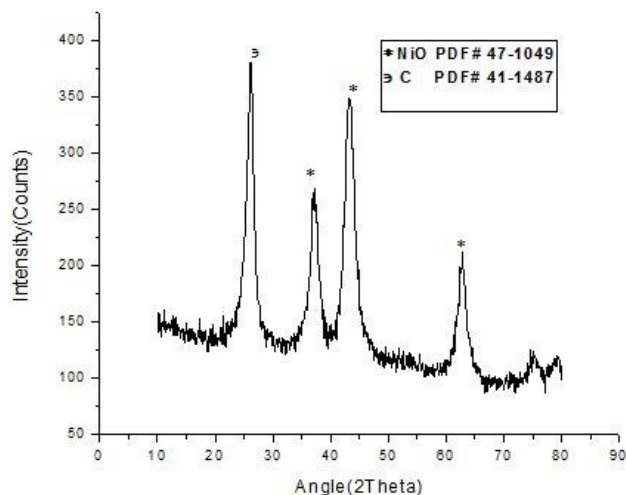


Figure 49: XRD analysis of NiO-CNTs

The peak at angle  $26^{\circ}$  matches the peak of CNT and other three peaks matches the peaks of NiO as discussed in NiO section. The results better explain the phase of the material and explain about its exact phase form.

#### 5.1.4 Morphology of deposited films:

The films are deposited on ITO coated PET. The SEM and EDS analysis is performed on ITO coated PET. The samples are coated with gold to make the surface more conductive so that better images could be captured at high magnification. The SEM images of NiO-CNTs deposited on ITO coated PET are in the Figure 50 and Figure 51.

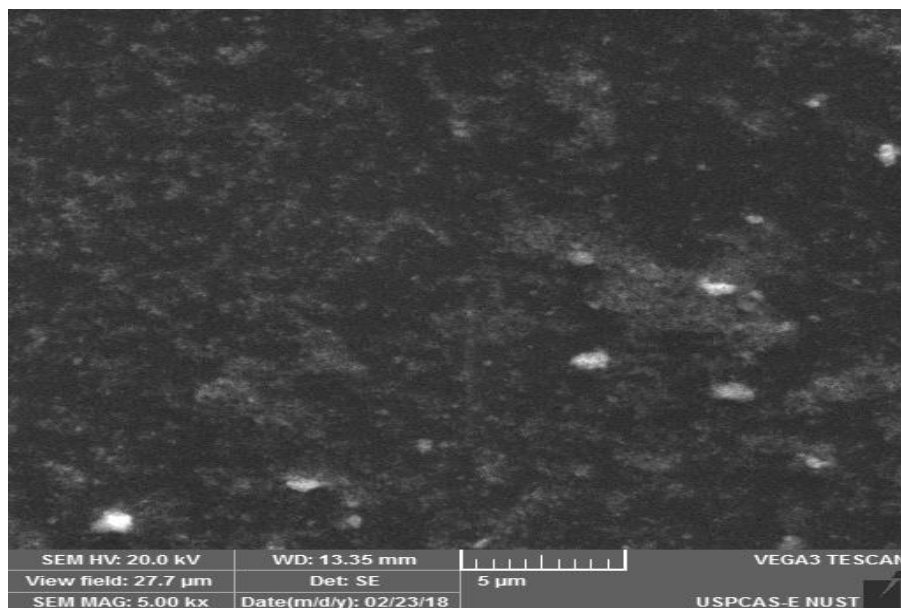


Figure 50: SEM of NiO-CNTs at 5um

Above image is at low resolution around 5um while the other SEM is taken at 500nm resolution to get more detailed analysis of the deposited film.

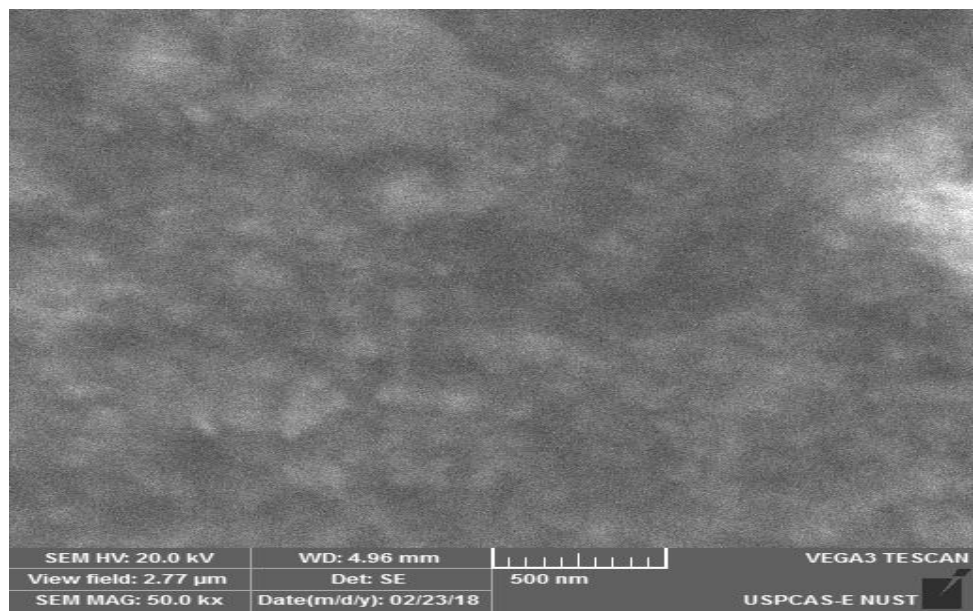


Figure 51: SEM image of NiO-CNTs deposited on PET at 500nm

The above images gets blur due to high resolution.

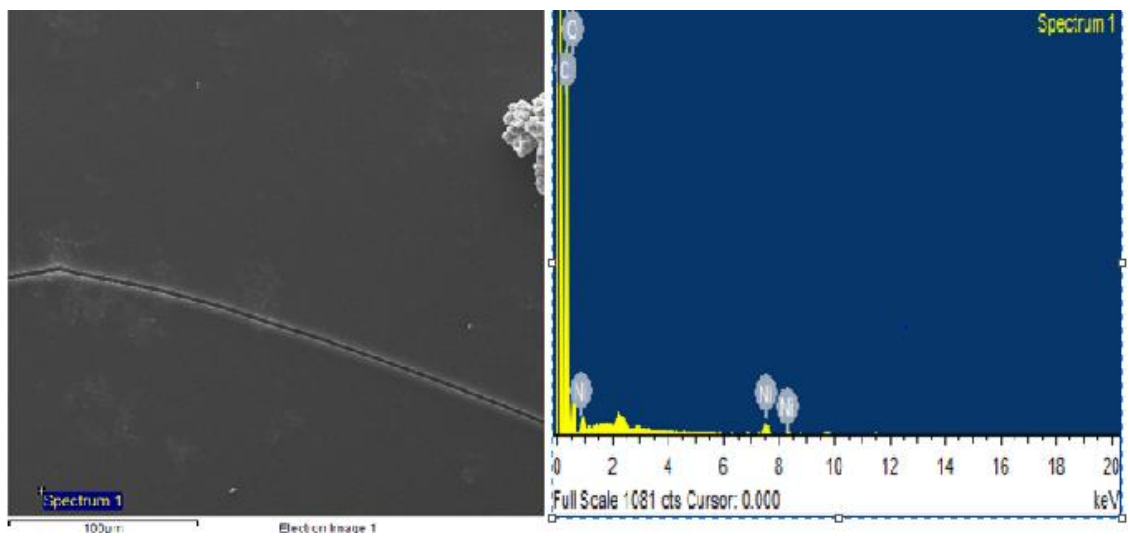


Figure 52:EDS analysis of NiO-CNTs

Table 6: Compositional *analysis of NiO-CNTs coated film*

Element	Weight%	Atomic%
C K	68.75	87.10
O K	13.20	12.55
Ni K	1.32	0.34
Totals	83.27	

## 5.2 UV-Vis spectroscopy analysis:

UV-VIS spectroscopy is used to find the transmittance of the counter electrode in my research. Transmittance is very important factor of solar cell to use them in buildings as transparent/semitransparent windows. Below is the comparison of transmittance of all three materials based counter electrodes.

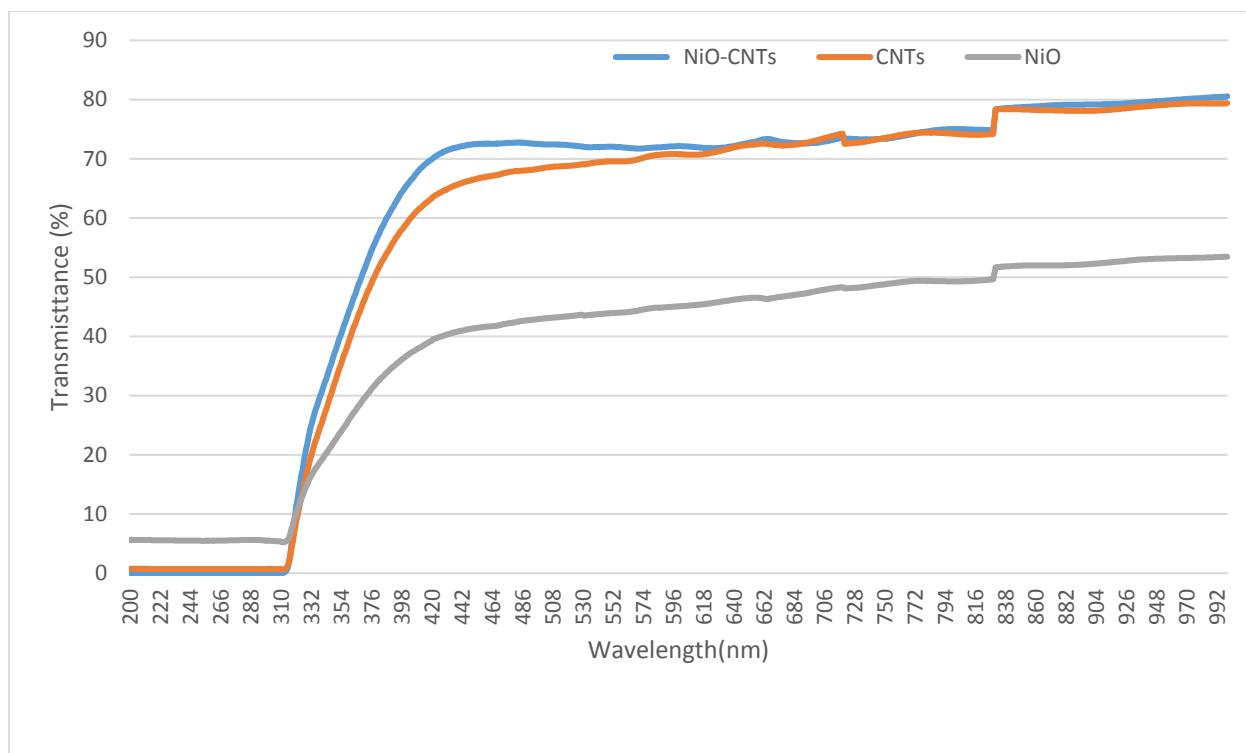


Figure 53: Transparency of NiO-CNTs, CNTs and NiO based counter electrode

The graph above shows that NiO-CNTs based counter electrode is more transparent as compared to NiO and CNTs alone. Thus by using NiO-CNTs transparent dye sensitized solar cells can be fabricated.

### 5.3 Electrochemical analysis by cyclic voltammetry

Electrochemical properties of counter electrode are very important in dye sensitized solar cell. To determine electrochemical properties of counter electrode, graph is plotted current versus voltage.

CV analysis is performed on NiO, NiO-CNTs and CNTs materials. The purpose is to compare the electrochemical properties and analyze the better option for counter electrode of dye-sensitized solar cells.

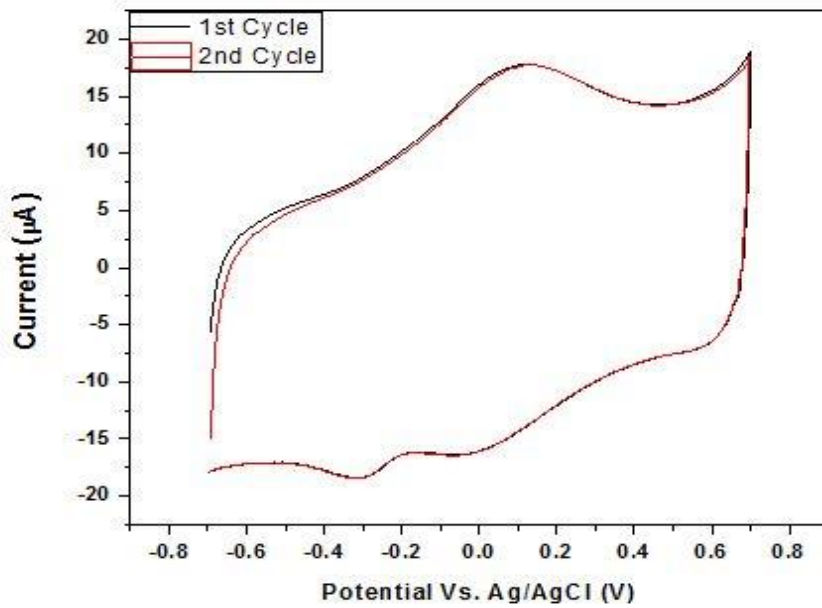


Figure 54: CV results of NiO

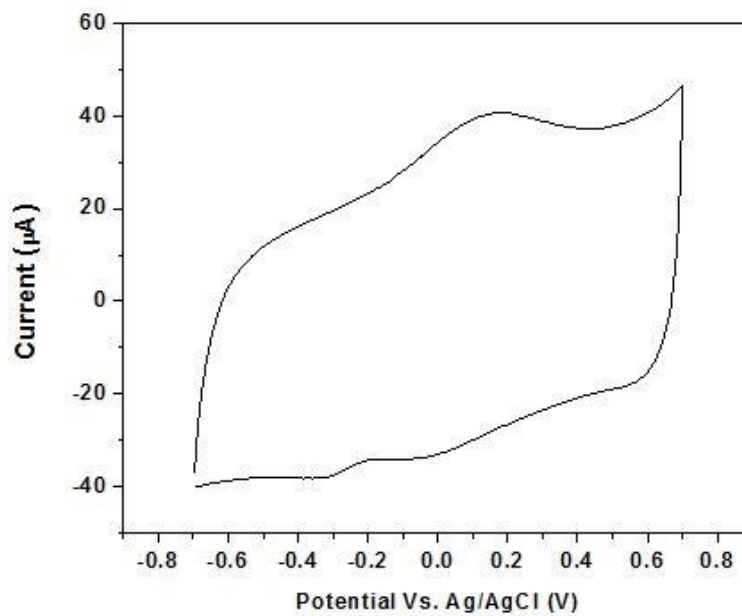


Figure 55: CV result of CNTs

The Figure 54 is result of CV analysis of NiO. The experiment is run for two cycles. The current reaches up to 18uA.

Applied voltage is kept between 0.8 V and -0.8 V as solution is aqueous and it above 1V aqueous solution start splitting.

The Figure 55 is result cyclic voltammetry of CNTs as counter electrode. The graph clearly shows that as compared to NiO from the previous Figure the current is high as voltage is increased. Voltage is varied between +0.7V and -0.7V. Current vary between -40uA and 40uA when voltage is applied. Due to applied voltage, current flow and the amount of current tell about properties of counter electrode.

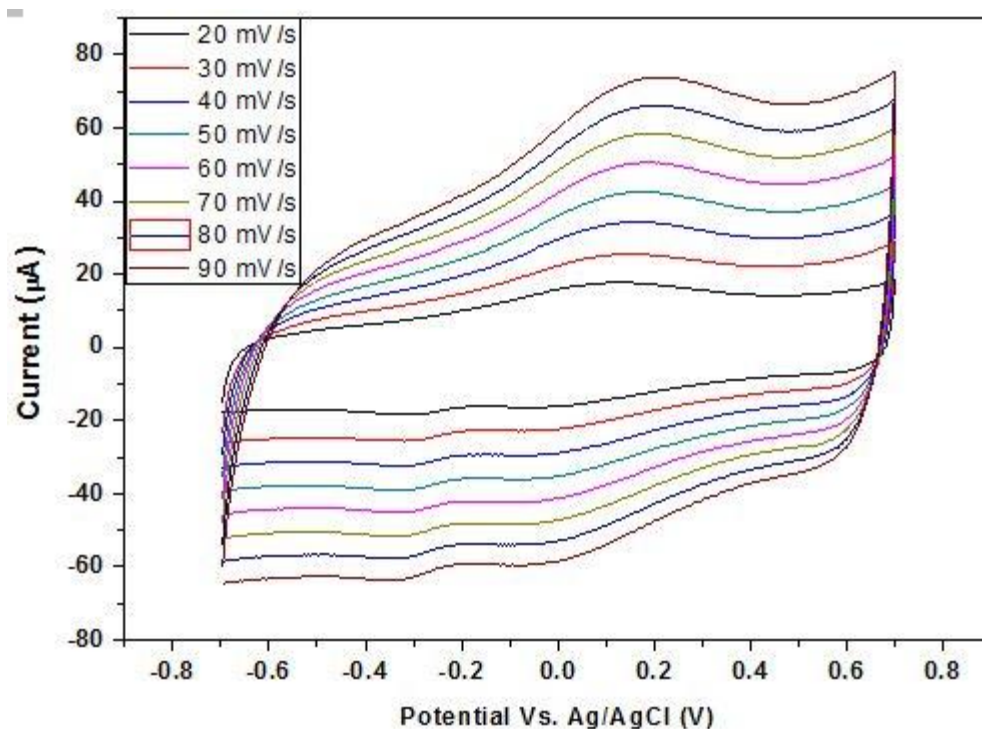


Figure 56: CV result of NiO-CNTs

The Figure 56 is cyclic voltammetry result of NiO-CNTs. The sample is analyzed at multiple scan rate. The graph clearly shows the better performance of NiO-CNTs as compared to NiO and CNTs.

By increasing the scan rate, reaction time is reduced thus recombination is reduced which results in higher current values. As the voltage is varied between -0.7V and 0.7V, the current varies between -65uA and 65uA which is much wider range than that of NiO and CNTs. Higher the current means lower resistance and thus electron will pass quickly at counter electrode. This would favor the reaction at counter electrode in case of NiO-CNTs as compared to NiO and CNTs [1].



The redox peak at the right side of the CV graph is related to the oxidation reaction which means conversion of tri iodide ion into iodide ion ( $I_3^- + 2e^- \rightarrow 3I^-$ ), which occurs at the CE of the DSSC and is vital for its operation; the left peaks corresponding to  $3I^- \rightarrow I_3^- + 2e^-$  and is insignificant in the context of DSSC. For analysis of catalytic performance of the cell, it is very important to find the peak-to-peak distance, peak cathode voltage and peak current density.

Left bottom of the CV results show the anode of the solar cell while the top right side of the Figure shows the cathode of the DSSC.

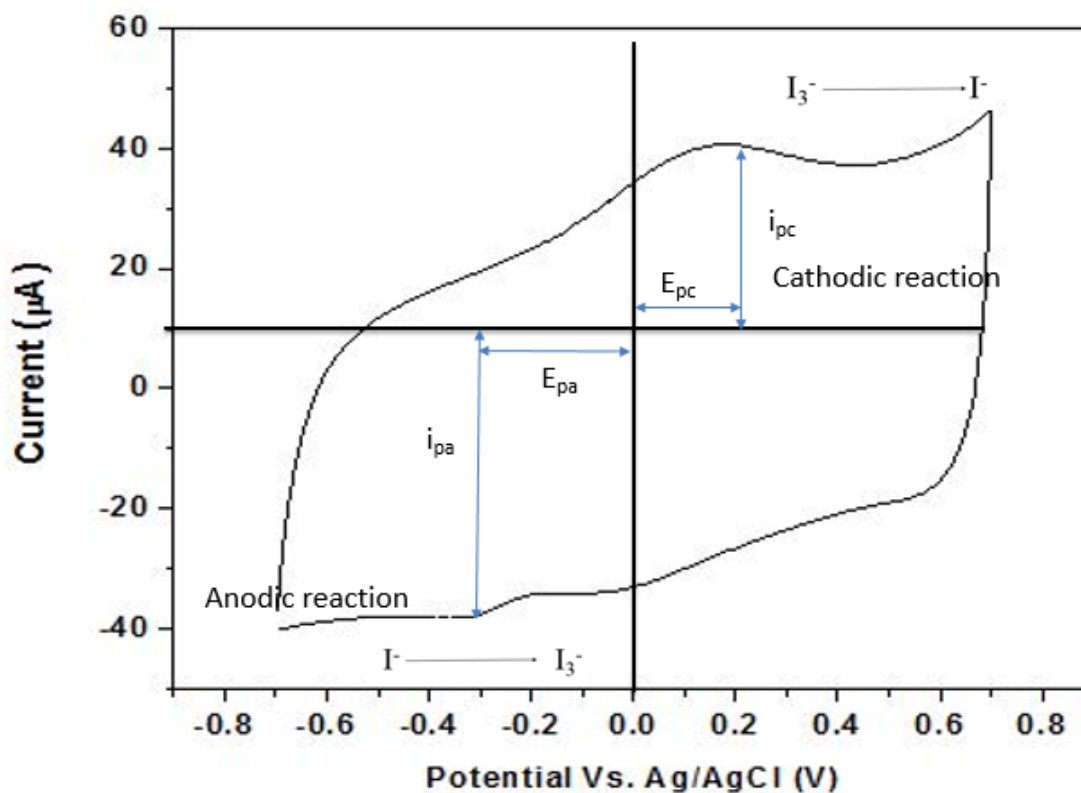


Figure 57: Cathodic and anodic reaction on CV curve

An efficient counter electrode should have low peak-to-peak distance and high current density. High current means reaction rate is high while low peak-to-peak potential difference means over potential is low. The Figure above shows the trend of increase of peaks with increase in scan rate. The voltage difference determine the reactivity of the electrode.

## 5.4 Electrical properties of deposited film by Hall Effect

Electrical properties of counter electrodes are very important to consider. Efficiency of solar cells depend on electrical properties of electrodes. Hall Effect analysis is used to find the conductivity, mobility and resistivity of the coated sample. In this study, Ecopia HMS-3000 is Hall Effect equipment, which is used for electrical analysis.

Table 7: comparison of properties on basis of Hall Effect

Material	Sheet resistance(ohm/cm)	Resistivity(ohm.cm)	Mobility (cm <sup>2</sup> /Vs)	Conductivity (1/ohm.cm)
NiO	2.52*10 <sup>9</sup>	2.52*10 <sup>6</sup>	3.78*10 <sup>-1</sup>	3.97*10 <sup>-7</sup>
CNTs	7.71*10 <sup>7</sup>	7.71*10 <sup>4</sup>	3.289	1.297*10 <sup>-5</sup>
NiO-CNTs	6.26*10 <sup>6</sup>	60.26*10 <sup>3</sup>	2.49*10 <sup>2</sup>	1.597*10 <sup>-4</sup>

The table 7 shows the resistivity, mobility and conductivity of coated film. This table shows that NiO-CNTs based film has high conductivity, high mobility and low resistance as compared to NiO and CNTs coated films. NiO-CNTs properties are much better than CNTs. The conductivity of NiO-CNTs coated film is more than ten times CNTs coated film. High conductivity of NiO-CNTs based counter electrode would leads to better efficiency of DSSC.

## 5.5 Efficiency comparison of DSSCs

Complete solar cells are assembled and characterized using IV measurement setup under 1.5 AM illumination. Output of IV measurement setup is in form of current and voltage curves. The results are plotted in the following figures.

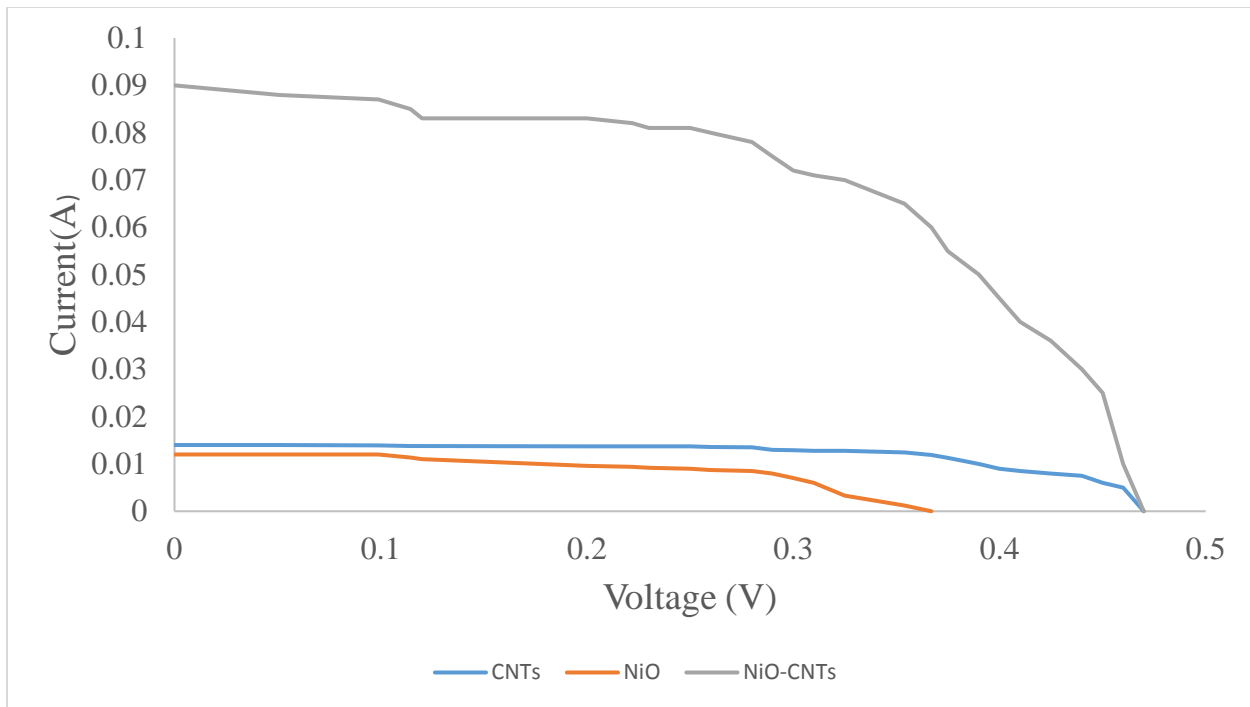


Figure 58: Comparison of IV measurement of NiO, CNTs and NiO-CNTs based DSSC

A comparison is made based on these results. Fill factor (FF), Voc, Isc, Vm and Im are derived for all three solar cells and reported in the table below. Power conversion efficiency (PCE) has also been calculated and compared in the same table.

Table 8: Comparison of DSSC based on counter electrode from NiO, CNTs and NiO-CNTs

	NiO	CNTs	NiO-CNTs
Voc	0.32	0.47	0.47
Isc	0.012	0.014	0.09
V <sub>m</sub>	0.25	0.35	0.3
I <sub>m</sub>	0.008	0.012	0.07
FF	52.08	42.87	49.56
PCE (%)	0.09	0.190	0.9545
Efficiency as compared to NiO	1	2.11	10.60

This table clearly shows that NiO-CNTs based DSSC performed much better as compared to NiO and CNTs based dye sensitized solar cell.

From Figure 58, Voc of NiO based DSSC is observed to be lower than other two counter electrode based DSSCs which shows that addition of CNTs in NiO has greatly enhanced the performance of electrode. Isc of DSSC based on NiO-CNTs composite is much higher than the other two counter electrode based solar cells. This effect can be related to higher electronic transportation and collection in composite in DSSC. In NiO chances of recombination are very high but with addition of CNTs, transport is being assisted thus recombination is reduced. Due to reduced recombination, electronic transportation is improved.

## Chapter summary

In this chapter characterization techniques are discussed in detail. Morphology of NiO, CNTs and NiO-CNTs composite are characterized using XRD analysis techniques. Peaks obtained from XRD analysis of NiO, CNTs and NiO-CNTs exactly matches the peaks of NiO, CNTs and NiO-CNTs SEM analysis is used to observe the structure of the material. SEM of NiO shows the nano structure of NiO. Similarly SEM analysis of CNTs show the nanotube structure of CNTs. The diameter of CNTs is a few nano meters. SEM analysis of NiO-CNTs show the nano structure of NiO and nanotube of carbon. EDS analysis confirms the percentages of Ni, Oxygen and carbon in NiO-CNTs which clear that composite is properly prepared. Hall Effect equipment is used to find the conductivity and charge mobility of the coated film. This shows that conductivity of NiO-CNTs composite is better than NiO and CNTs alone. Cyclic voltammetry is used to find the catalytic properties of NiO, CNTs and NiO-CNTs composite. The result shows that NiO-CNTs is better as compared to catalytic properties of NiO and CNTs. Complete solar cell is fabricated using microfluidic analysis. Complete DSSC is tested using IV profiler at AM 1.5.  $I_{sc}$ ,  $V_{oc}$ , FF and efficiency of solar cell is obtained. Comparison shows that NiO-CNTs based DSSCs are more efficient than NiO and CNTs.

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# Chapter 6: Conclusions and Proposed Future Work

## 6.1 Conclusion:

There are multiple conclusions based on the research. These conclusions are given below.

1. Carbon Nano-materials are highly conductive and low cost as compared to platinum so it CNTs could replace Pt for fabrication of counter electrode of dye-sensitized solar cells.
2. Preparation the composite of CNTs with metal oxides like NiO improve the electrical and catalytic properties of CNTs
3. On basis of CV analysis and Hall effects results, it become clear that conductivity and electrochemical properties of NiO-CNTs are better as compared to CNTs and NiO alone.
4. Efficiency of NiO-CNTs is better than NiO and CNTs alone.
5. Cost of carbon Nano-materials is much less as compared to platinum so it would be cost efficient to use carbon Nano-materials and metal oxide composites for DSSCs. This is also a goal to get low cost substitution of platinum.

## 6.2 proposed future works:

Multiple metals composites can be prepared with carbon nanotubes (CNTs) and the counter electrode can be fabricated through these metal CNTs composites. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) also provide better insight of the counter electrode working.

Moreover, the comparison can be made by varying the thickness of deposition layer of composite on a conductive surface as well. Some organic materials based counter electrodes could also be fabricated. Recently multiple fruits wastes are used for this purpose in china and many other countries. Waste is being used in better way instead of polluting the environment.





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