B. TECH. PROJECT REPORT

On

1D SnO_2 Nanorods for Energy Conversion Applications

BY

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DISCIPLINE OF MATERIAL SCIENCE AND METALLURGICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY INDORE

December 2019

1D SnO$_2$ Nanorods for Energy Conversion Applications

A PROJECT REPORT

Submitted in partial fulfillment of the
requirements for the award of the degrees

of
BACHELOR OF TECHNOLOGY
in

MATERIAL SCIENCE AND METALLURGICAL ENGINEERING

Submitted by:
Shreyas S S

Guided by:
Dr. Rupesh S Devan

INDIAN INSTITUTE OF TECHNOLOGY INDORE
DECEMBER 2019

CANDIDATE'S DECLARATION

We hereby declare that the project entitled **"1D SnO_2 Nanorods for Energy Conversion Applications"** submitted in partial fulfillment for the award of the degree of Bachelor of Technology in 'Material Science and Metallurgical Engineering' completed under the supervision of **Dr. Rupesh S. Devan (Associate Professor).** IIT Indore is an authentic work.

Further, I declare that I have not submitted this work for the award of any other degree elsewhere.

SHREYAS S S

CERTIFICATE by BTP Guide(s)

It is certified that the above statement made by the students is correct to the best of my knowledge.

Dr. RUPESH S. DEVAN
(Asociate Professor)

Preface

This report on “1D SnO_2 Nanorods for Energy Conversion Applications" is prepared under the guidance of Dr. Rupesh S. Devan.

Through this report, we have tried to synthesize 1D nanorods by the use of SnO_2 and control the uniformity by varying parameters such as concentration etc. Nanorods have been grown using hydrothermal process. We have tried to optimize properties of Electron Transport layer and performed characterizations to verify them. Various characterization techniques such as XRD, FESEM, EDS, etc.

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Acknowledgements

I take this opportunity to express my deep sense of respect and gratitude for Dr. Rupesh S. Devan for believing in me to carry out this work under his supervision. His constant encouragement, friendly interactions, and constructive support have enabled this work to achieve its present form. His innovative perspective towards things and his continuous pursuit for perfection has had a profound effect on me and has transformed me majorly. I feel greatly privileged to be one of his students.

I am thankful to IIT Indore for giving me an opportunity to carry out the research work and providing all the facilities. Very special thanks to Prof. Pradeep Mathur, Director, IIT Indore, for supporting and providing us facilities to perform my work smoothly here.

I am extremely thankful to my mentor Mr. Vishesh Manjunath for guiding and helping me out from the very first day I joined this project.

Lastly, but undoubtedly the most valued, gratitude is expressed for my parents, guardians for letting me choose my dreams and supporting me endlessly. Your un-matched support made this work possible.

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Abstract

With the rapid increase of efficiency up to 23.32% during the past few years, hybrid organic-inorganic metal halide perovskite solar cells (PSCs) have become a research “hot spot” for many solar cell researchers. Organic-inorganic hybrid perovskite solar cells have developed rapidly in recent years owing to the low-cost and high power conversion efficiency. The perovskite materials show various advantages such as long carrier diffusion lengths, widely-tunable bandgap with great light absorption potential. The low-cost fabrication techniques together with the high efficiency make PSCs comparable with Si-based solar cells. The excellent performance of PSCs is attributed to the superior electrical properties of each layer, including the electron transport layer ETL, light-harvest layer, hole transport layer. As one of the most promising electron transport layer materials for perovskite solar cells, SnO_2 shows excellent transmission in visible range, an appropriate energy band gap, a deep conduction band level, and high electron mobility, leading to efficient electron extraction and transport. SnO_2 is regarded as an effective electron transport material for attaining high-performance perovskite solar cells. In this project, vertically aligned SnO_2 nanorod arrays are grown directly on fluorine-doped tin oxide substrates in an acidic solution via hydrothermal method. X-ray diffraction, field emission scanning electron microscopy, UV- Vis absorption spectroscopy was used to determine the intrinsic characteristic properties of the as grown SnO_2 nanorods. The x-ray diffraction peaks revealed high phase purity of the as grown SnO_2 nanorods. Further, the uniform growth of nanorods over the complete substrate was probed with electron microscopy. Gold nanoparticles (Au NPs) were coated on SnO_2 nanorods to introduce the plasmonic effect to synergystically increase the plasmonic resonance spectrum and the required absorption spectrum of the perovskite layer for achieving light trapping in thin film solar cells.

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Chapter 1

Introduction

1. Background

Solar energy in one form or another is the source of nearly all energy on the earth. Humans, like all other animals and plants, rely on the sun for warmth and food. The world is facing energy crises and looking for an alternative utilizing solar energy. The need for energy is increasing with each progressing day with the increase in population. At the same time, the depletion of fossil fuels is escalating. Therefore, the world needs alternate sources to produce energy to meet energy short fall around the world. For example, fossil fuels, plant matter from a past geological age, is used for transportation and electricity generation and is essentially just stored solar energy from millions of years ago. The potential for solar energy is enormous, since about 200,000 times the world's total daily electric-generating capacity is received by Earth every day in the form of solar energy. Unfortunately, though solar energy itself is free, the high cost of its collection, conversion, and storage still limit its exploitation in many places. Solar radiation can be converted either into thermal energy (heat) or into electrical energy, though the former is easier to accomplish.

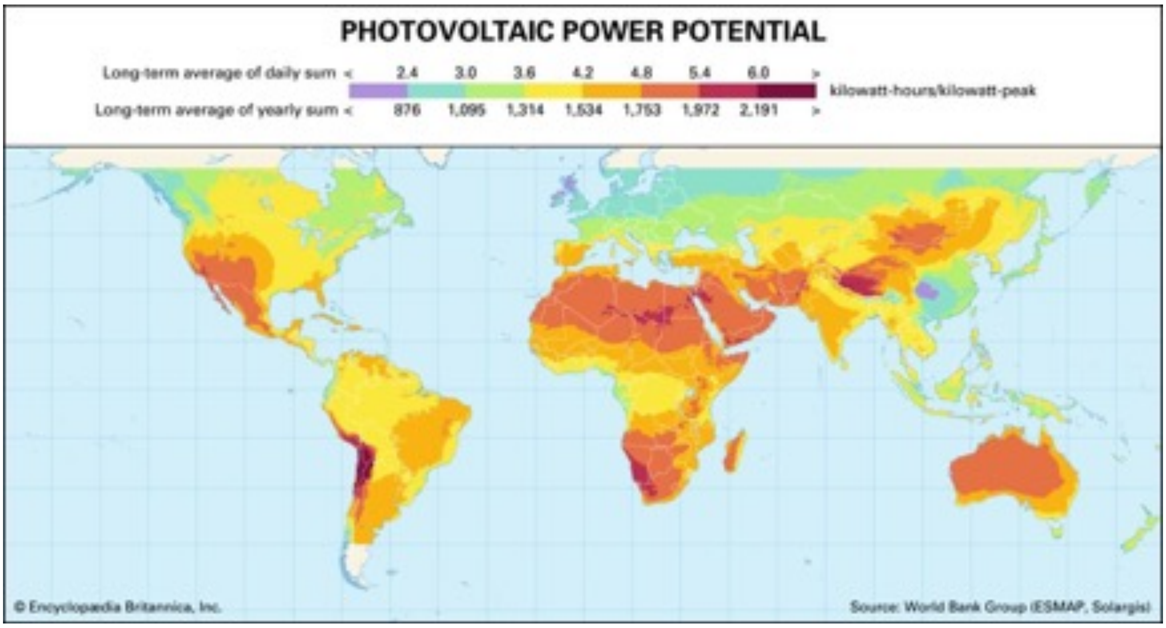

Figure 1. Earth's photovoltaic power potential.

Three practical ways to extract maximum benefits from this unlimited natural re- source are:

1. Photovoltaic Systems (PV systems): Photovoltaic (PV) modules, often referred to as solar panels, are the most ubiquitous solar power harvesting technology. PV modules generate electricity by energizing electrons inside their material system. PV modules are made from semiconductor materials, which can absorb sunlight and create electric energy. When sunlight is absorbed in a semiconductor, the optical energy of the light is transferred to the electrons inside the material. The energized electrons can then be extracted from the semiconductor into an electrical circuit, yielding electricity. A significant reason why semiconductor materials are used for PV modules is their ability to separate electrons into high and low energy states, which are separated by an energy gap (band gap) that is inherent to the material.
   Advantages:

    - Affordable and nearly everyone can adopt.
    - It is eco-friendly.
    - Enhance the resiliency and reliability of the electricity supply.
    - Long-time warranty and low maintenance cost.

2. Solar Thermal: Solar thermal, also know concentrating solar power (CSP), is a lesser-known method to extract solar power. In CSP, sunlight is directed using mirrors and then concentrated at a single point. The concentrated solar energy is then used on a working liquid to generate steam. The high-energy steam then turns a turbine generator to produce electricity. The different inherent difference between solar thermal and traditional power plants is that CSP uses renewable energy input to generate steam.

3. Artificial Photosynthesis: Artificial photosynthesis intends to mimic the process of natural photosynthesis and to increase the energy conversion ef-

ficiency by replacing the biological agents in the natural scheme with solid-state materials that drive chemical reactions to produce the desired fuels. The principal of artificial photosynthesis is based on electrochemistry. Many naturally occurring chemical reactions generate electricity with a distinct voltage. This phenomenon was the scientific basis used to engineer some of the world's first battery systems. Unlike PV modules, the electricity is not extracted into an external circuit but used to initiate chemical reactions at the surface of the material. The chemical reactions can be accelerated with certain catalyst materials, which increase the energy conversion of the overall system when engineered expertly.

2. Classification of Photovoltaic Solar Cells

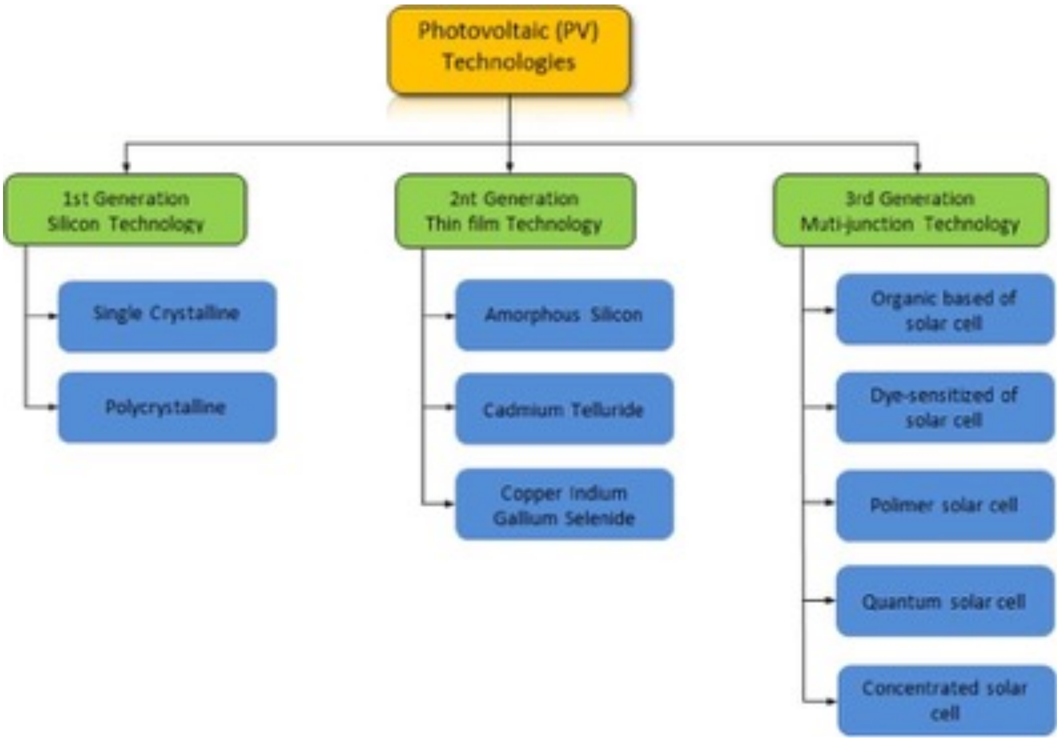

Figure 2. Classification of photovoltaic technologies

Though the photovoltaic effect was first observed in 1839 by Alexandre-Edmond Becquerel, the first modern solar cell was patented by Russel Ohl in 1946. In 1954 Bell Laboratories found that silicon doped with certain impurities was very sensitive to light. This signaled the start of the modern age of solar power technology. This signaled the start of the modern age of solar power technology.

Based on different technologies and materials, the solar cells can also be grouped into three different generations:

2.1. First generation solar cells

The cell consists of a large-area, single-crystal, single layer p-n junction diode, capable of generating usable electrical energy from light sources with the wavelengths of sunlight. The cells are typically made using a diffusion process with silicon wafers. These silicon wafer-based solar cells are the dominant technology in the commercial production of solar cells, accounting for more than 86% of the terrestrial solar cell market.

2.2. Second Generation Solar Cells

These cells are based on the use of thin epitaxial deposits of semiconductors on lattice-matched wafers. There are two classes of epitaxial photovoltaics - space and terrestrial. Space cells typically have higher AM0 efficiencies (28-30%) in production, but have a higher cost per watt. Their thin-film cousins have been developed using lower-cost processes, but have lower AM0 efficiencies (7-9%) in production. There are currently a number of technologies/semiconductor materials under investigation or in mass production. Examples include amorphous silicon, polycrystalline silicon, micro-crystalline silicon, cadmium telluride, copper indium selenide/sulfide. An advantage of thin-film technology theoretically results in reduced mass so it allows fitting panels on light or flexible materials, even textiles. Second generation solar cells now comprise a small segment of the terrestrial photovoltaic market, and approximately 90% of the space market.

2.3. Third Generation Solar Cells

They are proposed to be very different from the previous semiconductor devices as they do not rely on a traditional p-n junction to separate photogenerated charge carriers. For space applications quantum well devices (quantum dots, quantum ropes, etc.) and devices incorporating carbon nanotubes are being studied - with a potential for up to 45% AM0 production efficiency. For terrestrial applications, these new devices include photoelectrochemical cells, polymer solar cells, nanocrystal solar cells, Dye-sensitized solar cells and are still in the research phase.

2.4. Tandem Solar Cells

One method to increase the efficiency of a solar cell is to split the spectrum and use a solar cell that is optimised to each section of the spectrum. Tandem solar cells can either be individual cells or connected in series. Series connected cells are simpler to fabricate but the current is the same though each cell so this contrains the band gaps that can be used. The most common arrangement for tandem cells is to grow them monolithically so that all the cells are grown as layers on the on substrate and tunnel junctions connect the individual cells.

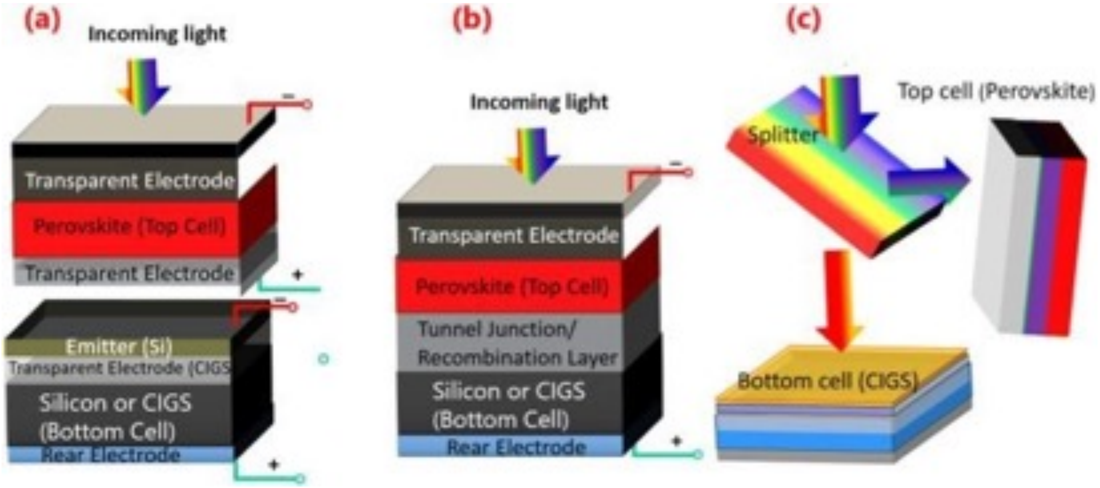

Figure 4. Tandem perovskite solar cells

3. Perovskite Solar Cell

Perovskite solar cells aim to increase efficiency and lower the cost of solar energy. A perovskite solar cell is a type of solar cell that includes a perovskite structured compound, most commonly a hybrid organic-inorganic lead or tin halide-based material, as the light-harvesting active layer. Perovskite PVs indeed hold promise for high efficiencies, as well as low potential material & reduced processing costs. A big advantage perovskite PVs have over conventional solar technology is that they can react to various wavelengths of light, which lets them convert more of the sunlight that reaches them into electricity. The organic-inorganic halide perovskite solar cells (PSCs) have attracted a great deal of attention of solar cell research community due to an incredible device efficiency improvement from 3.8% to

22.1% since 2009. The perovskite already gained much attention as a potential replacement of the silicon PV devices, which is still occupied the most dominant position in the current PV market, with record efficiency of about 26%. This small gap of solar cell efficiency attracted recent attention especially from the researchers with experience in dye-sensitized solar cells (DSSCs) or organic solar cells because some materials can be used in both PSCs and organic solar cells. The structure of PSCs also origins from the device structure of DSSCs. The perovskite materials have been demonstrated with largely tunable band gap (e.g., $CH_3NH_3PbX_3$ has a band gap from 1.5 eV to 2.3 eV) and great light absorption coefficient, which is similar to other thin film solar cell materials such as CdTe and copper zinc tin sulfide. Its low-cost and convenient fabrication techniques also serve as the possible advantages over silicon-based devices that require complicated and costly high-vacuum deposition methods. Reports of successful cell fabrication on flexible substrates even indicated a greater possibility to the large-scale roll-to-roll manufacturing of PSCs that can be used in the industries.

3.1. Solar Cell Efficiency

The surge in power conversion efficiency of perovskite solar cells is shown in the NREL data provided below as compared to other PV technologies. High efficiency of ~23 % is achieved by tailoring properties of the perovskite absorbers, which are discussed below.

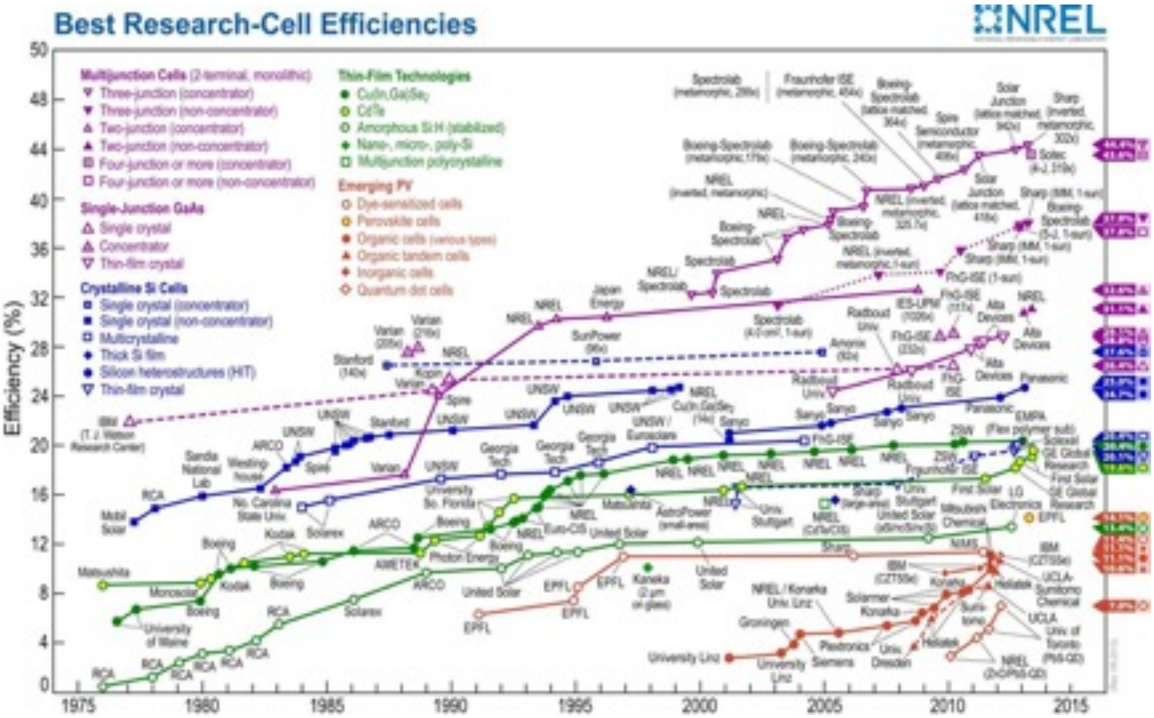

Figure 5. Solar cell efficiencies

3.2. Crystal Structure of perovskite absorber

Generally, perovskites have the general formula ABX_3 where, A and B are two cations of very different sizes and X is an anion that bonds to both. X is often oxygen but also other large ions such as halides, sulfides and nitrides are possible.The A site cation is slightly larger than B cation. The B atom has 6 fold coordination number and the A atom have 12 fold. In general, Divalent A cations are 12 fold coordinated by oxygen anions and sits in corners of the cube at corner position (0, 0, 0). The tetravalent B cations lie within oxygen octahedral, occupies the body center position (½, ½, ½). The oxygen atoms are at the face center of the cubic lattice at position (½, ½, 0).

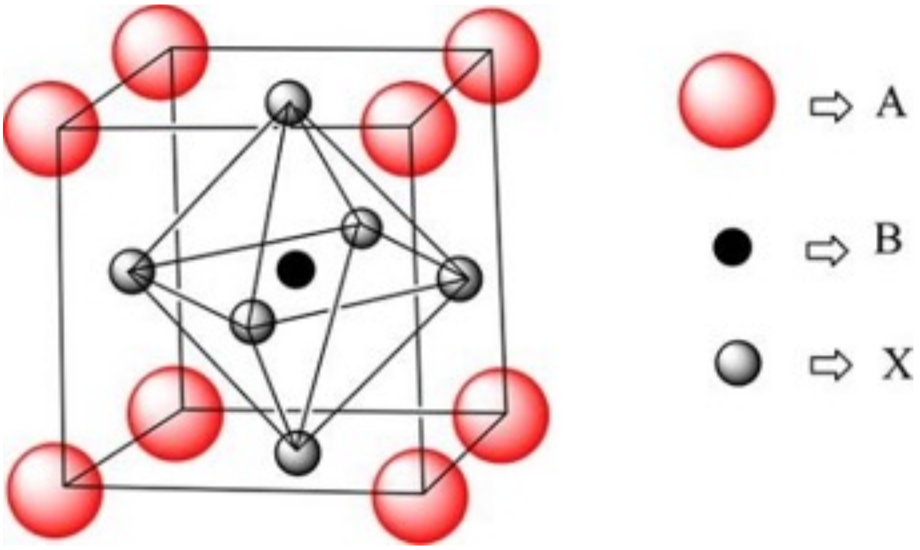

Figure 6. Crystal structure of perovskite

Perovskite materials have different phases depending on the change of temperature. When temperature is lower than 100 K, the perovskite displayed a stable orthorhombic (γ) phase. With temperature increased to 160 K, the tetragonal (β) phase started to appear and replace the original orthorhombic (γ) phase . As temperature increases further to about 330 K, the tetragonal (β) phase started being replaced by another stable cubic (α) phase.

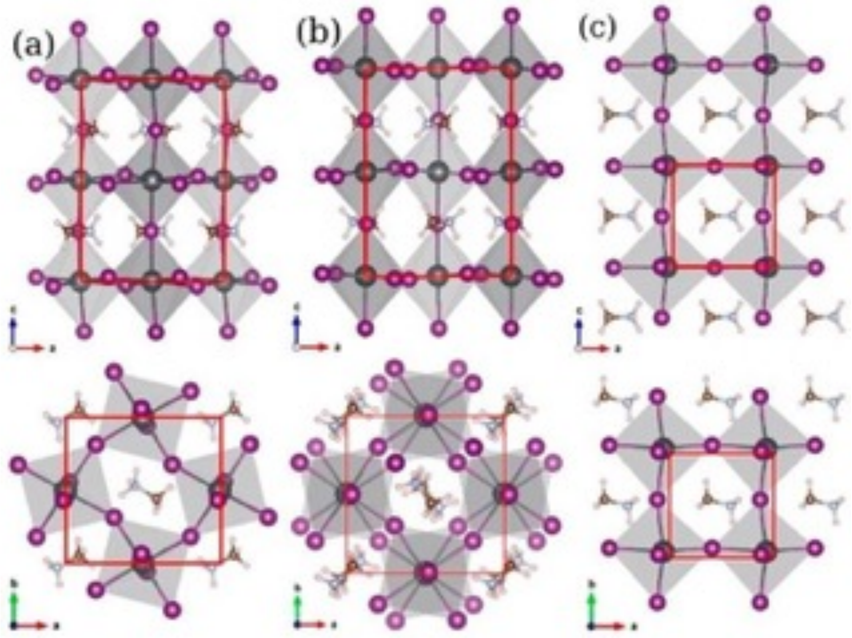

Figure 7. Comparison of (a) orthorhombic; (b) tetragonal and (c) cubic perovskite phases

Organometallic halide perovskites include an organic cation (e.g., methyl-ammonium CH_3NH_3+, ethyl-ammonium $CH_3CH_2NH_3+$, formamidinium $NH_2CH=NH_2+$), a metal cation of carbon family (i.e., Ge^{2+}, Sn^{2+}, Pb^{2+}) and a halogen anion (i.e., F^-, Cl^-, Br^-, I^-). Among them, methyl-ammonium-lead-iodide ($MAPbI_3$) is the most widely used perovskite light absorber. Some recent research efforts also replaced lead with other metal ions due to the concern of toxicity of lead during device fabrication, especially for the future large-scale manufacturing . In addition, several organic cations ($CH_3NH_3^+$ and $NH_2CH=NH_2^+$), inorganic cations (Cs^{2+} and Sn^{2+}) and halide anions (Br^-, Cl^- and I^-) have been used to improve the efficiency and stability.

3.3. Device Structure

Planar and mesoscopic structure-based cells have efficiency of 20.8% and 21.6%, respectively. A schematic of both planar and mesoscopic structure could be found in Figure 8. The PCSs can be fabricated in both sequences rather than thin-film PV, whose device configuration was limited by the properties of absorber materials. Thus, there are four major types of PSCs: substrate/superstrate-configured mesoporous structure and substrate/superstrate-configured planar structure.

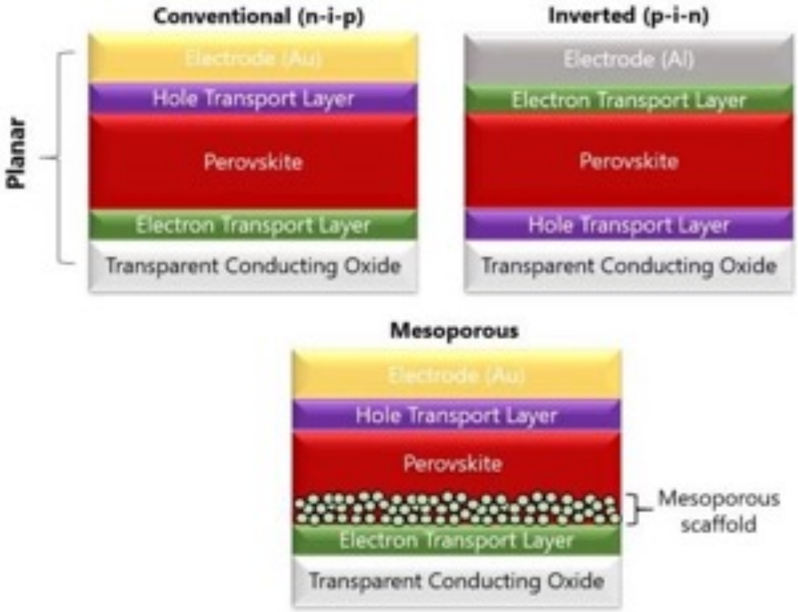

Figure 8. Schematic diagrams of mesoscopic and planar perovskite solar cells (PSCs)

The most typical n-i-p mesoporous structure is the first demonstrated high-efficient structure for perovskite devices. Started with the TCO cathode (mostly fluorine-doped tin oxide, FTO), a thin compact blocking layer was applied to decrease shunting, a mesoporous metal oxide layer filled with highly crystalline perovskite absorber layer. A layer of HTM was applied and a metal contact layer was deposited on the top of the device.

3.4. Perovskite Layer Fabrication

Spin-coating is the most widely used method in the fabrication of PSCs but it is not suitable for large-scale manufacturing. However, thermal evaporation is the only vacuum-based methods that ever been demonstrated with a good cell performance. To the best of our knowledge, sputtering was never used possibly due to the lack of appropriate sputtering target and the possible damage of high-energy species to the unstable perovskite materials.The fabrication techniques of PSCs can be differentiated into one-step process; two-steps process; vapor-assisted process and thermal evaporation process.

3.4.1. One-step process

A precursor solution (such as a mix of CH_3NH_3I and PbI_2) is coated that then converts to the perovskite film upon heating.

3.4.2. Two-steps process

In the two-step process, the metal halide (such as PbI_2) and organic components (such as CH_3NH_3I) are spin-coated in separate, subsequent films.

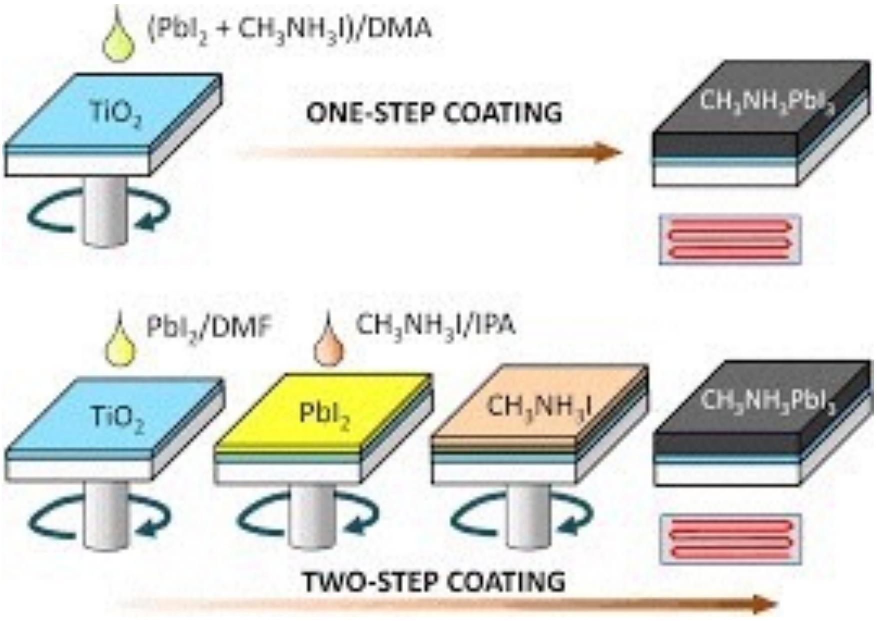

Figure 9. Fabrication methods of perovskite

3.4.3. Vapor-Assisted Solution Method

Vapor-assisted solution method could be considered as a modified two-step method. During the second step, vaporized MAI/FAI reacted with PbI_2 to form perovskite phase after further film annealing. This method successfully avoids the partial perovskite dissolving especially during the dipping process.

3.4.4. Thermal Vapor Deposition

The first reported thermal-vapor-deposited perovskite was reported by Mitzi et al. . Liu et al. applied a co-evaporation with sources of MAI and $PbCl_2/PbI_2$ on rotated substrate and they fabricated a planar structure PSC of 15.4%. A further research unveiled that during co-evaporation, the reaction between $PbCl_2$ and MAI tended to form PbI_2 at first, then transferred into $MAPbI_2$ under continuous MAI incorporation. Finally, the residual MAI would be found in a form of $MAPbI_3 \cdot xMAI$.

3.5. Components of Solar Cell

Perovskite solar cells are third generation multilayer thin film solar cells. Transparent Conductive Oxide, Electron transport layer, Absorbing layer, hole transport layer, and metal contacts are the main component of a solar cell. Here we will discuss these components in details.

3.5.1. Transparent Conductive Oxide (TCO)

Transparent conductive oxides (TCO) are doped metal oxides used in optoelectronic devices such as flat panel displays and photovoltaics (including inorganic devices, organic devices, and dye-sensitized solar cell). Most of these films are fabricated with polycrystalline or amorphous microstructures. Mobility in these films is typically limited by ionized impurity scattering due to the large amount of ionized dopant atoms and is on the order of 40 $cm^2/(V \cdot s)$ for the best performing TCOs. Current transparent conducting oxides used in industry are primarily n-type conductors, meaning their primary conduction is as donors of electrons. They are typically grown on a glass substrate and used as a conducting layer for photovoltaic applications. They have lower resistivity of around 10^{-4} Ω.cm and high transmittance >85%. Their electrical conductivity is greater than 1000 S/cm, which makes them ideal for use in optoelectronics devices because of efficient charge carrier transportation. Fluorine doped Tin Oxide (FTO) and Indium doped Tin Oxide (ITO) are the two rigid transparent conductive layers used in PCSs.

3.5.2. Electron transport layer (ETL)

The electron transport layer plays a vital function in extracting and transporting photogenerated electrons, modifying the interface, aligning the interfacial energy level and minimizing the charge recombination in perovskite solar cells. The electron transport layer plays an important role in extracting and transporting photogenerated electrons from the perovskite layer to the cathode or anode. At the same time, the ETL also modifies the interface between the perovskite layer and the electrode, minimizing charge recombination. Here we are using 1-D SnO_2 nano-rods architecture as an electron transport material for solar cell fabrication.

3.5.3. Perovskite layer

Perovskite has an optimum bandgap of 1.2-2.1 eV which makes them good absorber over the visible spectrum along with unique properties like high charge diffusion length, low surface recombination velocity, tunable band gap, high electron and hole mobility which makes them ideal for photovoltaic application. They also show ambipolar characteristics and therefore HTM free solar cell fabrication is also possible .

3.5.4. Hole transport layer (HTM)

HTM is used to assist the transportation of holes generated in the absorbing layer to the metal contact. It only allows holes to pass through this and by blocking the electron it prevents short circuiting of the device. HTL mainly serves three purposes. First, deposited prior to the gold electrode, it avoids direct contact of the metal electrode with the mesoporous SnO_2 -perovskite layer, and therefore increases the selectivity of the contact. This reduces recombination as evident from an increased open-circuit voltage and a higher luminescence efficiency. Second, the HTL increases the internal quantum efficiency independent of applied voltage and illumination wavelength by reducing (diffusion) losses of charges. Third, due to a smoothing of the SnO_2-perovskite mesoscopic layer the HTL increases the reflectivity of the gold electrode, allowing for a second path of the light through the absorber. Both effects result in an enhancement of the short-circuit current density.

4. Solar cell parameters

4.1. Open Circuit Voltage (V_{oc})

The open-circuit voltage, V_{oc} is the maximum voltage available from a solar cell, and this occurs at zero current. The open-circuit voltage corresponds to the amount of forward bias on the solar cell due to the bias of the solar cell junction with the light-generated current. An equation for V_{oc} is found by setting the net current equal to zero in the solar cell equation to give:

$$V = (\eta/q)\ln[I_{ph}/I_0]$$

where, T = Temperature (^{o}K)

η = Ideality factor

k = Boltzman constant

I_{ph}= Photon current

I_O = Dark saturation current

4.2. Short circuit current (I_{sc})

The short-circuit current is the current through the solar cell when the voltage across the solar cell is zero (i.e., when the solar cell is short circuited).The short-circuit current is due to the generation and collection of light-generated carriers. For an ideal solar cell at most moderate resistive loss mechanisms, the short-circuit current and the light-generated current are identical. Therefore, the short-circuit current is the largest current which may be drawn from the solar cell.The equation for the short-circuit current can be approximated as:

$$I_{sc} = qG(L_n+L_p)$$

where G is the generation rate, and Ln and Lp are the electron and hole diffusion lengths respectively.

4.3. Fill factor (FF)

The short-circuit current and the open-circuit voltage are the maximum current and voltage respectively from a solar cell. However, at both of these operating points, the power from the solar cell is zero. The "fill factor", more commonly known by its abbreviation "FF", is a parameter which, in conjunction with V_{oc} and I_{sc}, determines the maximum power from a solar cell. The FF is defined as the ratio of the maximum power from the solar cell to the product of V_{oc} and I_{sc} so that:

$$FF = P_{MP}/(Voc\ Isc)$$

$$FF = (V_{MP} I_{MP})/(V_{OC}\ I_{SC})$$

4.4. Efficiency (η)

Efficiency is defined as the ratio of energy output from the solar cell to input energy from the sun. In addition to reflecting the performance of the solar cell itself, the efficiency depends on the spectrum and intensity of the incident sunlight and the temperature of the solar cell. Terrestrial solar cells are measured under AM1.5 conditions and at a temperature of 25°C. Solar cells intended for space use are measured under AM0 conditions.

$$\eta = (V_{OC} I_{SC} FF)/P_{IN}$$

where:
Voc is the open-circuit voltage;
Isc is the short-circuit current;
FF is the fill factor and
η is the efficiency.

5. Absorption coefficient

The absorption coefficient determines how far into a material light of a particular wavelength can penetrate before it is absorbed. The absorption coefficient depends on the material and the wavelength of light which is being absorbed. Semiconductor materials have a sharp edge in their absorption coefficient, since light which has energy below the band gap does not have sufficient energy to excite an electron into the conduction band from the valence band. The absorption coefficient for several semiconductor materials is shown below.

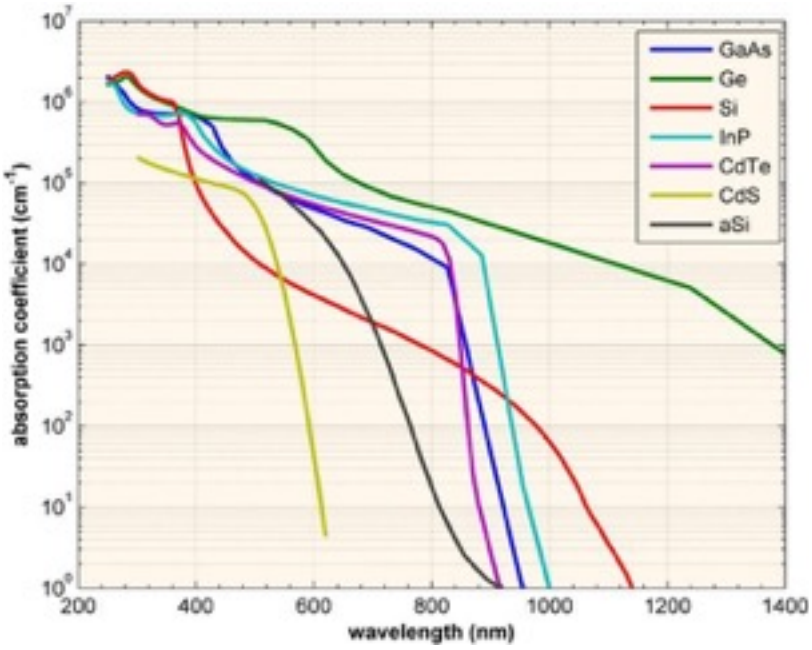

Figure 10. absorption spectrum

6. Tunable optimum bandgap

The semiconductor chosen for a solar cell has to absorb as much of the solar spectrum as possible, therefore a low band gap is desireable. However, this is counter balanced by the desire to also have as large a built-in voltage as possible which requires a larger band gap. Therefore as a compromise, a band gap between 1.0 and 1.7 eV makes an effective solar semiconductor. The bandgap of these semiconductors can be tuned by strain-inducing from tunable sizes and shapes due to quantum confinement effects. A larger tunable bandgap range is possible due to the high elastic limit of semiconducting nanostructures and perovskite material. The perovskite has a tunable band-gap, that can be controlled with halide substitution (for example), they tend to be considered as the best solution for more efficient solar cells. Their ability to be solution-processed or vapour-deposited would allow benefiting high quality scalable inexpensive integration on existing devices.

7. Long charge diffusion length

The diffusion length of a carrier type in a material can be defined as the average distance that an excited carrier will travel before recombining.

The diffusion length is related to the carrier lifetime by the diffusivity according to the following formula:

$$L = \sqrt{D\tau}$$

where:

L is the diffusion length;

D is the diffusivity and

τ is the lifetime in seconds.

The minority carrier lifetime and the diffusion length depend strongly on the type and magnitude of recombination processes in the semiconductor. Perovskites has high charge carrier mobility which enables long charge carrier diffusion lengths.

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Chapter 2

Review of Past Work and Problem formulation

This chapter gives insight about the recent developments in the field of PSCs. It also highlights various kinds of solar cells technology and different methods for device fabrication used by researchers on this topic. A PSC is a type of solar cell which includes a perovskite structured compound, most commonly a hybrid organic-inorganic lead or tin halide-based material, as the light-harvesting active layer.

Alkali metal lead and halides like tin halides was already synthesized in 1893, yet the first crystallographic studies that proved that caesium lead halides had a perovskite structure with the chemical formula $CsPbX_3$ (X = Cl, Br or I) were only carried out 64 years later by the Danish scientist ChristianMøller. He observed that these coloured materials were photoconductive and suggested that they behave as semiconductors. In 1978, Dieter Weber replaced caesium with methylammonium cations ($CH_3NH_3^+$) to generate the first three-dimensional organic–inorganic hybrid perovskites. In 2009, Tsutomu Miyasaka and colleagues in Japan reported on organic–inorganic lead halide perovskite compounds as light absorbers in dye-sensitized solar cells. However, as the device delivered just 3.8% power conversion efficiency, had an active area of 0.24 cm^2 and was stable for only a few minutes, these initial results presented uncertainties about the likely deployment of these materials in photovoltaics.In 2012, the groups of Michael Grätzel in Switzerland and Nam-Gyu Park in South Korea demonstrated solid-state perovskite photovoltaic devices that overcame the poor stability of the material in liquid-based dye-sensitized solar cells. Later in the same year, Henry Snaith and colleagues in the United Kingdom demonstrated that the materials are not only able to sensitize a semiconductor, but also, and more interestingly, can themselves transport electronic charges to the solar cell electrodes, enabling higher device efficiencies

Nam-Gyu Park and his group in south korea demonstrated solid-state perovskite photovoltaic devices that overcame the poor stability of the material in liquid-based dye-sensitized solar cells. They produced perovskite NPs by the reaction of methylammonium iodide with PbI_2 and depositing it onto a submicron-thick mesoscopic TiO_2 film, whose pores were infiltrated with the hole-conductor spiro-MeOTAD. Illumination with standard AM-1.5 sunlight generated a large photo-currents (J_{SC}) exceeding 17 mA/cm^2, an open circuit photovoltage (V_{OC}) of 0.888 V and a fill factor (FF) of 0.62 yielding a power conversion efficiency (PCE) of 9.7%, the highest reported to date for such cells.

Michael Gratzel and his group in Switzerland demonstrated a concept of multi-functional molecular modulation of scalable and operationally stable perovskite solar cells which exhibit exceptional solar-to-electric power conversion efficiencies. The efficiently designed bi-functional molecular modulator SN links the mercapto-tetrazolium and phenylammonium moieties, which passivated the surface defects, while displaying a structure-directing function through interaction with the perovskite that induces the formation of large grain crystals of high electronic quality of the most thermally stable formamidinium cesium mixed lead iodide perovskite formulation.

Detao Liu and Yafei Wang and group in 2019 reviewed various configurations of SnO_2 based PSCs and assessed composite SnO_2 with other metal oxides and found out that the SnO_2−based PSCs are not only show much more stable and excellent in performance compared with TiO_2−based PSCs, but also can be prepared by the low−temperature process. Therefore they concluded that SnO_2 is one of the most promising substitutes of TiO_2 and the SnO_2 −based PSCs have better performance and stability with more devoted effort.

Xiaokun Zhang and Yichuan Rui and their group grew vertically aligned SnO_2 nanorod arrays on fluorine-doped tin oxide (FTO) substrates in an acidic solution via hydrothermal method, where the area density of the nanorod arrays was tailored by varying the precursor concentration.They could achieve the best power conversion efficiency of 15.46% which was attributed to acceleration of electron transport and decreased recombination rate at SnO_2/perovskite interface.

List of papers reviewed during the completion of the project

1. SnO_2-Based Perovskite Solar Cells: Configuration Design and Performance Improvement by De tao Liu, Yafei Wang in the year 2019.
2. Facile Fabrication of SnO_2 Nanorod Arrays Films as Electron Transporting Layer for Perovskite Solar Cells by Yinhua Lv, Peng Wang in the year 2018.

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Chapter 3

Objective

Solar power is the key to a clean energy future. Every day, the sun gives off far more energy than we need to power everything on earth.

1. Advantages:

- Renewable: Solar panels produce electricity by transforming the continuous flow of energy from the sun to electricity.
- CO_2-free: No harmful emissions are released into the air when electricity is produced by solar panels.
- Low operating costs: The photovoltaic process that transforms sunlight into electricity does not require any fuel and has no variable costs.
- Limitless solar energy: The sun provides more than enough energy to meet the whole world's energy needs, and unlike fossil fuels, it will not run out anytime soon. As a renewable energy source, the only limitation of solar power is our ability to turn it into electricity in an efficient and cost-effective way.
- Solar energy - a clean source: No greenhouse gas emissions are released into the atmosphere when solar panels to create electricity.
- No fuel to burn: After solar panels have been installed, operational costs are quite low compared to other forms of power generation. Fuel is not required, and this means that solar power can create large amounts of electricity without the uncertainty and expense of securing a fuel supply.

2. TW Challenge

Presently, relying on nuclear energy, we would require thousands of reactors to sustain energy demand. Sun is a huge source of energy.1.2×10^5 TW delivered to earth, and $36x10^3$ TW delivered on land. Annual human production of energy is about $4.6x10^{20}$ which is roughly 60 seconds of sunlight. Hence efficient utilization of solar energy is necessary.

3. SnO_2 Electron Transport Layer

TiO_2 is the most widely used materials as the ETL for PSCs. It has a bandgap of 3.6 eV and the wide bandgap guarantees the transmittance of the most light in the visible range. Additionally, the energy level matches with the perovskite band structure well, and the PSCs with the highest PCE record are based on this material. SnO_2 is a promising alternative to TiO_2 due to its perfect optical and electronic properties. First of all, SnO2 has a much higher electron mobility (421.70 cm/(V s)) than TiO_2, and it can ensure the efficient transport of electrons, thus, most of PSCs based on SnO_2 do not need nanostructures. Secondly, SnO_2 also has a wider energy bandgap compared with TiO_2, resulting in better transmittance and less light energy loss in PSCs. The wider bandgap also makes the ETL more stable under UV illumination. Thirdly, ITO and fluorine-doped tin oxide (FTO) consist of SnO_X. It means that there is smaller refractive index gradient between the TCO and SnO_2 compared with TiO_2, which can reduce the reflection of light. Last but not the least, the annealing temperature for SnO_2 film is lower than 180 C, signifying that solar cells can be fabricated with a lower cost and thermal budget. Recently, vertically aligned one-dimensional (1D) nanorod arrays have attracted researchers' interests, which incline to have fewer grain boundaries and exhibit advantages of unidirectional electron transport and enhanced charge collection. Nanorod arrays could also provide wider space for effective pore-filling with the perovskites as compared to the commonly used nanoparticle based mesoscale structure due to an open porous structure. Moreover, light scattering amongst the nanorod arrays is beneficial for improving the photon absorption efficiency of the perovskite layer. In the past, TiO_2 and ZnO nanorod arrays with tailored diameters, lengths as well as area densitie$_2$s were exploited as electron transport materials of the PSCs. Tin oxides with various chemical forms can be synthesized, including SnO_2, SnO, Sn_2O_3 and Sn_3O_4, with a variety of crystalline phases, such as orthorhombic, tetragonal, cubic, and triclinic crystals. Among the metal-oxides, tin oxide has attracted the most scientific attention because of its excellent properties, which make it suitable for use in opto-electronic devices, field emitters and gas sensors. SnO_2 doped with indium is used to make the renowned conductive transparent glass, indium tin oxide (ITO), which can be utilized for many applications, such as in optoelectronic and electrochromic devices. The 1D forms can enhance the unique properties of the material, making them suitable for a wide variety of applications such as biosensors, gas sensors, smart windows, solar cells, supercapacitors, photodetectors, light-emitting diodes, field emissions, and field-effect transistors. These 1D metal-oxide nanostructures have triggered a lot of excitement and allowed breakthrough achievements in all areas of electronics. In quest for a 1D morphology, tin oxides are synthesized in the form of nanorods, nanowires, nanobelts, zigzag nanobelts, nanoribbons, nanotubes, etc. Large-scale 1D SnO_2 nanorods/nanowires can be synthesized by the vapor-liquid-solid process with an Au catalyst at high temperatures. Peculiar 1D nanobelt-based SnO_2 nanozigzags can be synthesized by oxidizing Sn grains in an ambient atmosphere at high temperature. Physical Vapor Deposition (PVD), Confinement Growth, Lithographic Techniques, Glancing Angle Deposition is all types of Direct Physical Deposition Techniques that can be used to create 1D nanorods of metal oxide. Chemical Vapor Deposition, Hot-Filament Metal-Oxide Vapor Deposition, Sol-Gel Technique, Solvothermal Technique, Hydrothermal technique are all types of Direct Chemical Deposition Techniques.

Here in this project, we are adapting hydrothermal technique for the growth of SnO_2 nanorods. Hydrothermal synthesis includes the various techniques ofcrystallizing substances from high-temperature aqueous solutions at high vapor pressures. Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

The main objective of this project is to enhance the efficiency of perovskite solar cells by implementing one-dimensional (1D) SnO_2 nanorods as electron transport layer. An electron transport layer in an n-type layer used to create potential in the solar cell device along with the absorber and p-type material. Recently, vertically aligned 1D nanorod arrays have attracted researcher interest, which inclines to have fewer grain boundaries and exhibit advantages of unidirectional electron transport and enhanced charge collection. Nanorod arrays could also provide more extensive space for effective pore-filling with the perovskites as compared to the commonly used nanoparticle-based mesoscale structure due to an open porous structure. Moreover, light scattering amongst the nanorod arrays is beneficial for improving the photon absorption efficiency of the perovskite layer. In the past, TiO_2 and ZnO nanorod arrays with tailored diameters, lengths as well as area densities were exploited as electron transport materials of the PSCs. However, to the best of our knowledge, there have been few reports about PSCs using SnO_2 nanorod arrays as ETLs. PSCs based on SnO_2 nanoparticles as ETLs showed very high efficiencies and were almost free of hysteresis. Thus, the objective of the project is expected that by employing the 1D SnO_2 nanorod arrays as electron transport material would further improve the performance of PSCs. This project aims to synthesis tailored SnO_2 nanorod arrays on FTO glass by a facile hydrothermal method in the acidic solution. Further, hydrothermal method was adopted to gain complete control over the aspect ratio of the SnO_2 nanorods and followed by perovskite pore filling.

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Chapter 4

Experimental Section

1. Spin Coating

Spin coating is one of the most common techniques for applying thin films to substrates. Spin coating generally involves the application of a thin film (a few nm to a few um) evenly across the surface of a substrate by coating (casting) a solution of the desired material in a solvent (an "ink") while it is rotating. First the substrate is coated in the ink containing the molecules dissolved in a solvent .Then the substrate is rotated at high speed and the majority of the ink is flung off the side .Airflow then dries the majority of the solvent, leaving a plasticised film before the film fully dries to just leave the molecules on the surface .The rotation of the substrate at high speed (usually >10 rotations per second = 600 rpm) means that the centripetal force combined with the surface tension of the solution pulls the liquid coating into an even covering. During this time the solvent then evaporates to leave the desired material on the substrate in an even covering.

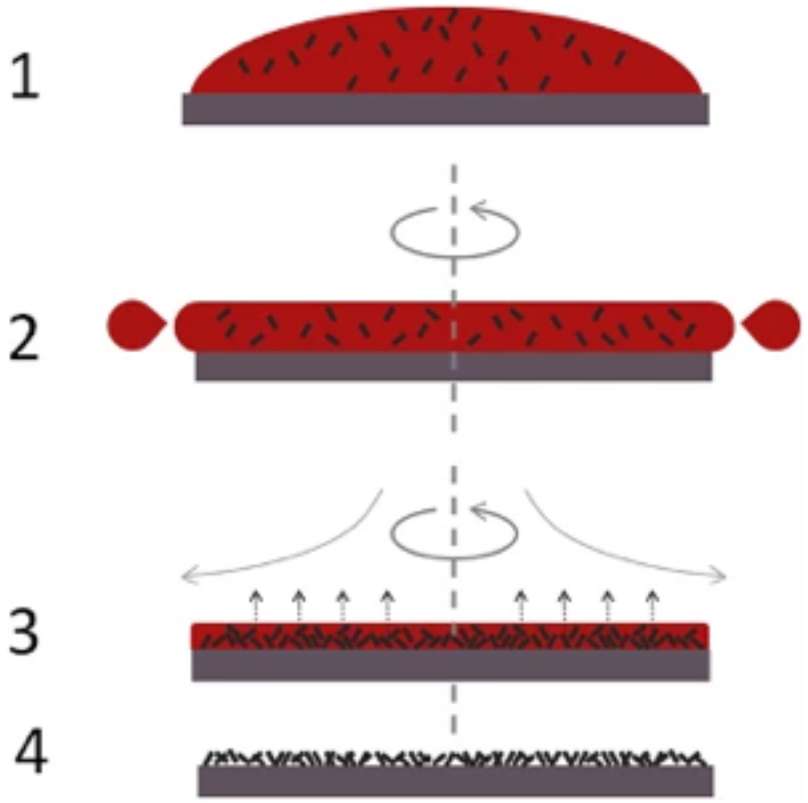

Figure 11. Example of spin coating a small molecule in solution using a static dispense.

2. Experimental methodology

Materials and reagents: Unless stated otherwise, all materials were purchased from Sigma Aldrich. Fluorine doped tin oxide (FTO) glass, SnO_2, HCl, Distilled water, ethanol.

Synthesis of SnO_2 nanorod arrays: The FTO conductive glass was sequentially cleaned in detergent solution, deionized water, and ethanol in an ultrasonic bath. Firstly, a compact seed layer was deposited on the FTO glass substrate by spin-coating. To prepare the seed solution, 0.1 M $SnCl_2$ $2H_2O$ isopropanol solution was refluxed at the temperature of 70 °C for one hour, and then aged for 6 h to form a transparent sol. Standard sample was prepared by dissolving 0.451gm of $SnCl_2.2H_20$ in 20 ml IPA (isopropanol). The seed layer was deposited onto FTO by spin coating steps at 2000rpm for 20 seconds and calcined at 500°C for 30 min. Secondly, SnO_2 nanorod arrays were grown on the seed layer via a hydrothermal method. Briefly, 25 mL of H_2O, 25 mL of ethanol and 2 mL of concentrated HCl were mixed in a teflon-lined autoclave, and the mixture was stirred at ambient conditions in magnetic stirrer for 5 min before the addition of $SnCl_4 \cdot 5H_2O$. Subsequently, one piece of seeded FTO substrate was placed in the teflon-lined autoclave. The hydrothermal reaction was performed at 200 °C for 12 h. After the hydrothermal reaction, the SnO_2 nanorod films were repeatedly rinsed with deionized water and ethanol to remove excess ions. Finally, the films were annealed at 500 °C for 30 min.

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Chapter 5

Characterization Techniques

1. X-Ray Diffraction Measurements

X-ray diffraction (XRD) is one of the most important non-destructive tools to analyze all kinds of matter—ranging from fluids, to powders and crystals. From research to production and engineering, XRD is an indispensable method for materials characterization and quality control. X-ray diffraction techniques are used for the identification of crystalline phases of various materials and the quantitative phase analysis subsequent to the identification. X-ray diffraction techniques are superior in elucidating the three-dimensional atomic structure of crystalline solids. The properties and functions of materials largely depend on the crystal structures. The Bragg equation, $n\lambda = 2d\sin\theta$ is one of the keystones in understanding X-ray diffraction. In this equation, n is an integer, λ is the characteristic wavelength of the X-rays impinging on the crystallize sample, d is the inter planar spacing between rows of atoms, and θ is the angle of the X-ray beam with respect to these planes. When this equation is satisfied, X-rays scattered by the atoms in the plane of a periodic structure are in phase and diffraction occurs in the direction defined by the angle θ. In the simplest instance, an X-ray diffraction experiment consists of a set of diffracted intensities and the angles at which they are observed.

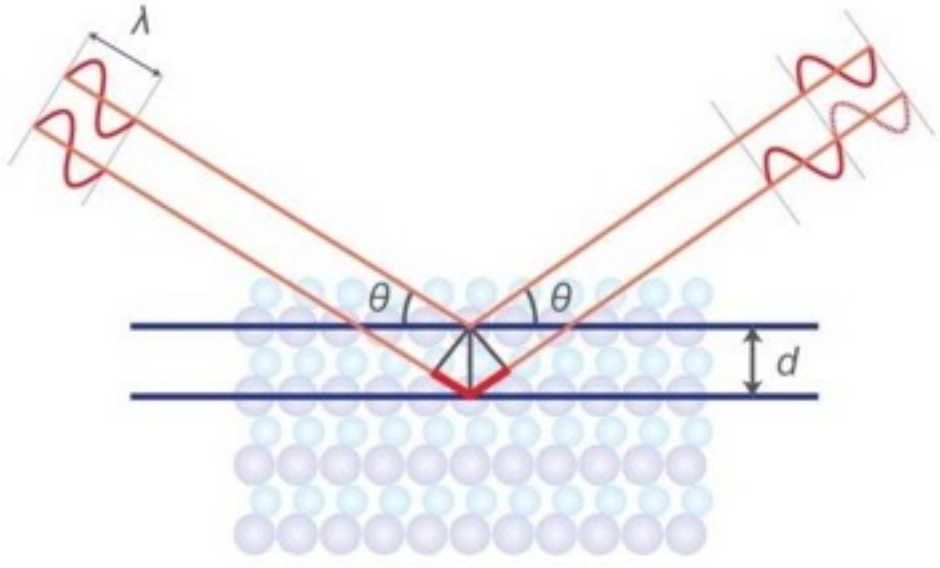

Figure 12. Bragg's Law

2. UV-Visible Spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. UV/Vis spectrophotometer is used in the quantitative determination of concentrations of the absorber in the solutions of transition metal ions and highly conjugated organic compounds. The instrument works on the basis of The Beer-Lambert law. The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. The absorbance changes with concentration.

Quantitatively, absorbance can be defined as

$A = -\log T = -\log (I_T/I_O)$

In the above equation, A is the absorbance, T is the transmittance, I_T and I_O are the intensities of the incident and transmitted light respectively. In a UV –Vis spectrometer deuterium lamp is used as a source of the incident light. The beam split- ter is used to split an incident beam in two ways. One beam is passed through the reference and another beam is passed through the sample. Photodiode converts these light waves into an electrical signal. The difference in intensities is detected by the detector placed at the end of the spectrometer. UV-Visible spectrometer works on three different modes. Absorbance, reflectance, and transmittance can be calculated by doing characterization in absorption mode, reflection mode, and transmission mode respectively.

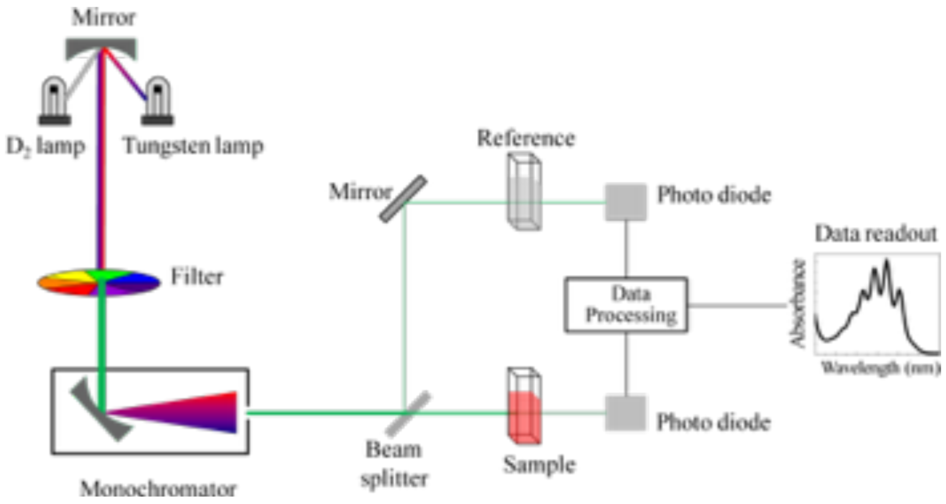

Figure 13. Schematic of the working set-up of UV-Vis spectrophotometer

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Chapter 6

Results and discussions:

1. XRD measurements

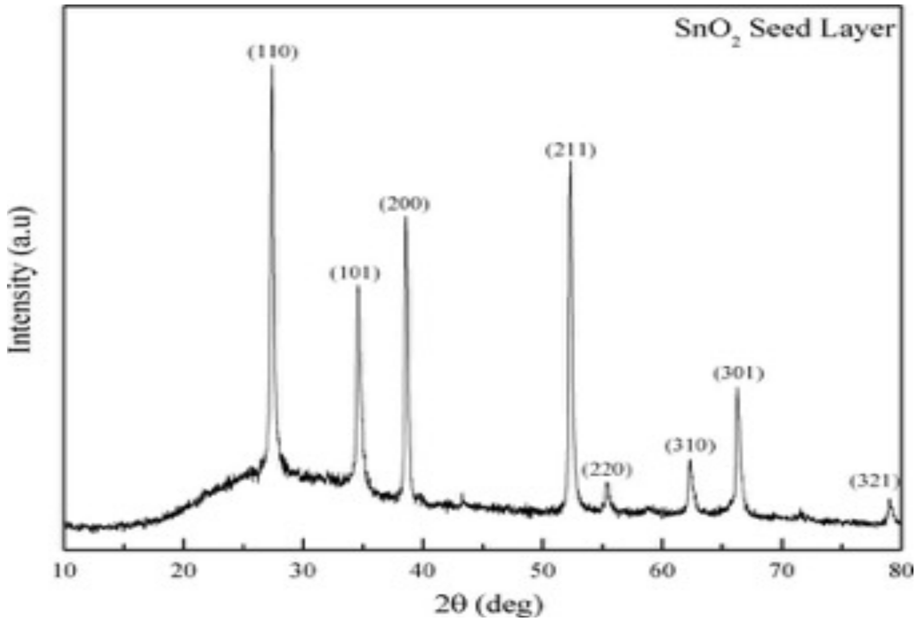

Figure 14. xrd of SnO$_2$ nanorods of SnO$_2$ of 0.1M concentration

X-ray Diffraction (XRD) was used to study the phase crystallinity and growth direction of SnO$_2$ nanorods. The XRD pattern of SnO$_2$ nanorods (Figure 14) synthesized using precursor concentration 0.1M shows tetragonal rutile structure. The pattern was matched with JCPDS Ref 21-1250 for SnO$_2$ and JCPDS Ref 82-2194 for FTO. The peak intensity value provides us the orientation of nanorod growth. From (figure 14), we can say that the orientation of nanorods is the direction of (110) plane.

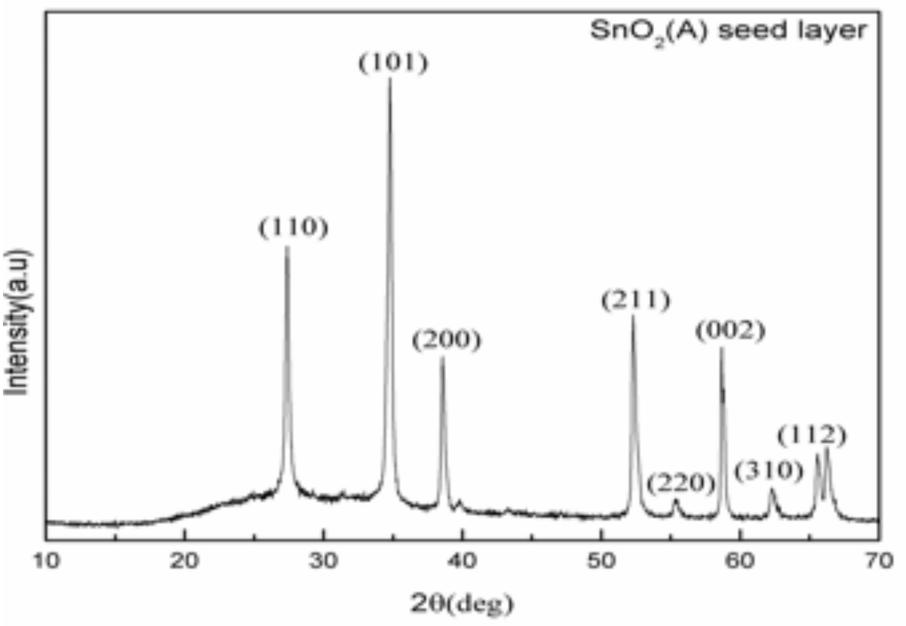

Figure 15. Xrd of SnO_2 nanorods of SnO_2 of 0.099M concentration of SnO_2

With the change in the concentration, we can observe that change in the intensity of peaks. The change in the concentration of precursor, the peak value changes but not peak position.

2. UV-Vis Spectroscopy

UV-Vis Spectroscopy is used to calculate the band gap of a material. Absorbtion increases as we move towards uv-visible region of wavelength near the 300nm wavelength and then decreases, i.e. the synthesized SnO_2 nanorod array are transparent to visible light. Such high transparency is a prerequisite to electron transport layer in n-i-p perovskite solar cell architecture.

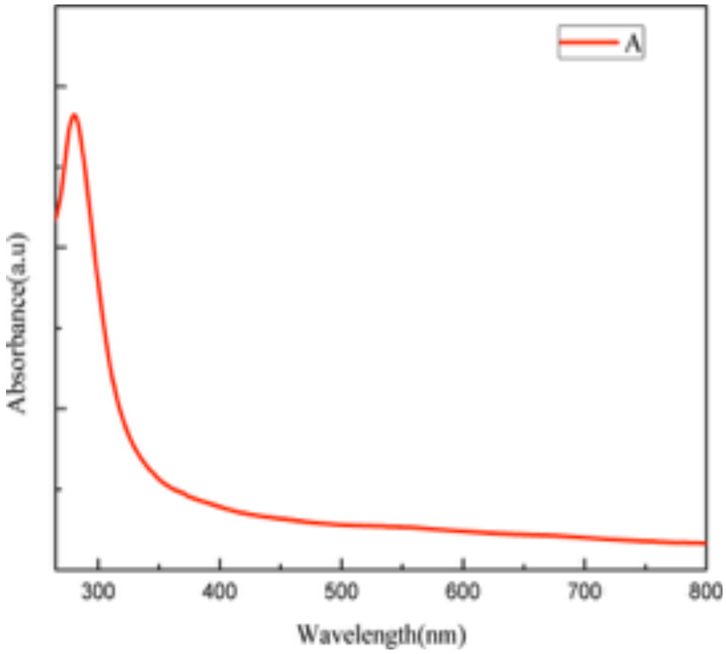

Figure 16. UV-Vis absorption spectra of SnO_2 nanorods.

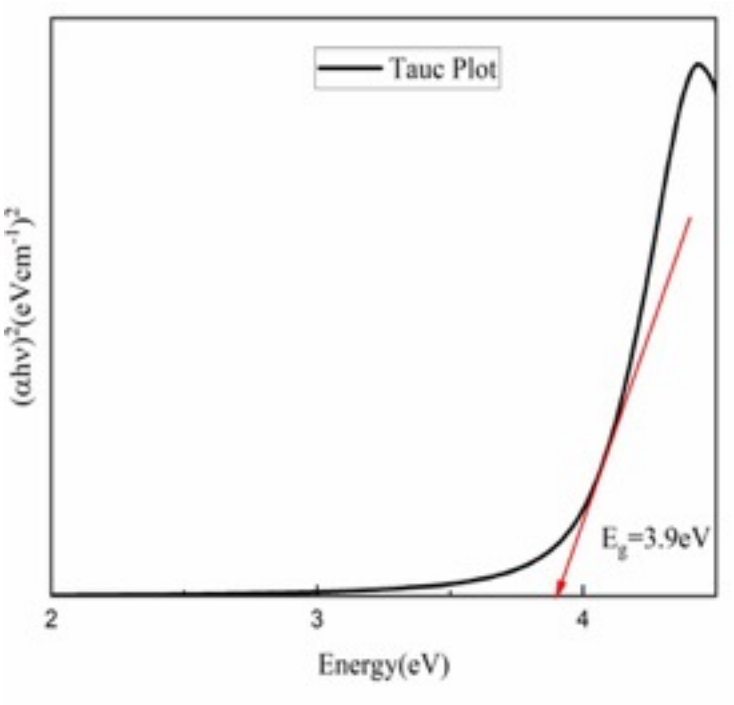

Figure 17. Tauc plot of absorbtion spectra of SnO_2 nanorods.

Figure 16 shows absorbtion spectra of SnO_2 nanorods. The material absorbs maximum light in the near the wavelength region of 300nm.The band gap of the SnO_2 nanorods obtained from this is approximately 3.9eV which shows us that the material is SnO_2.Band gap is calculated from tauc plot shown in the figure 17.

3. Photoluminescence Spectroscopy

PL spectroscopy is nondestructive method used to characterize the electronic structure of the material. Room temperature PL spectra of vertically grown SnO_2 nanorods and Au coated SnO_2 nanorods are shown in the figure 16 and 17 respectively. A broad emission spectrum is observed in the range of wavelength of 350nm - 500nm which lies in uv-visible range .Another small spectrum exists in the region of 650 nm-800 nm in the infrared region for both SnO_2 nanorods and Au coated SnO_2 nanorods.

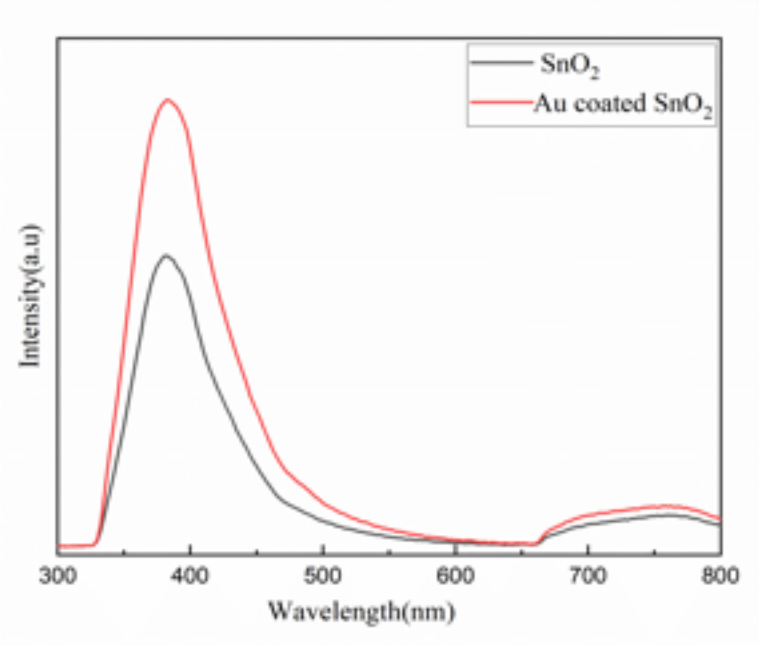

Figure 18. PL graph of SnO_2 nanorods and Au coated SnO_2 nanorods

As seen from the figure 18, it can be inferred that Intensity of gold coated SnO_2 photoluminescence higher than that of the plain SnO_2. Hence it can be inferred that gold coating increases absorbtion of the nanorods.

4. Energy dispersive X-Ray spectroscopy (EDS)

EDS is an analytical technique used to find the elemental composition of a sample. Here EDS analysis is done on SnO_2 nanorods sample to find the element along with the impurities present in the material.

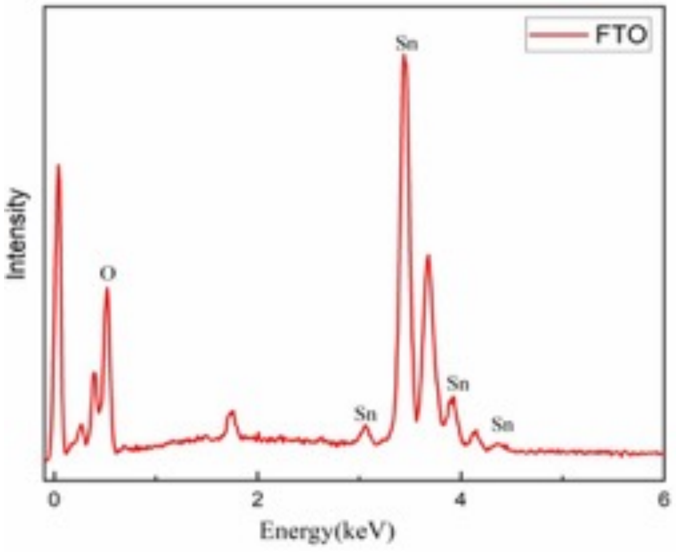

Figure 19. EDS plot of FTO

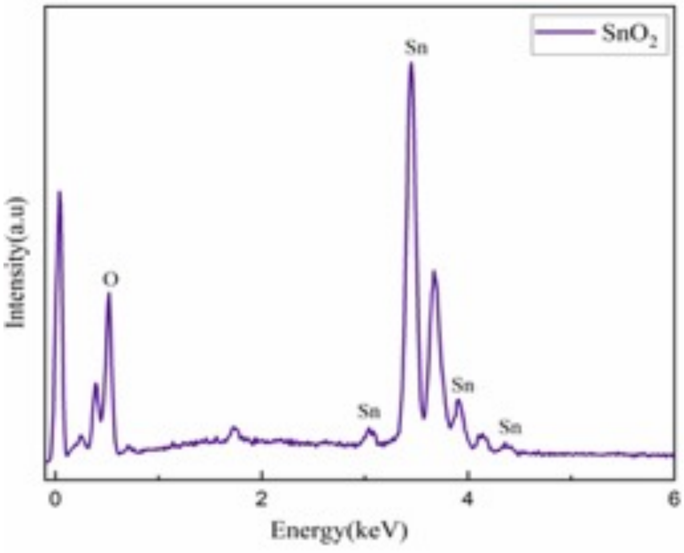

Figure 20. EDS plot of SnO_2 nanorods

From the figure 19 and 20, we can observe the EDS plot of FTO and SnO_2 nanorods. EDS pattern shows the presence of elements like Sn and O and a very small amount of Si and F from the underlying substrates.

5. FESEM analysis of nanorods:

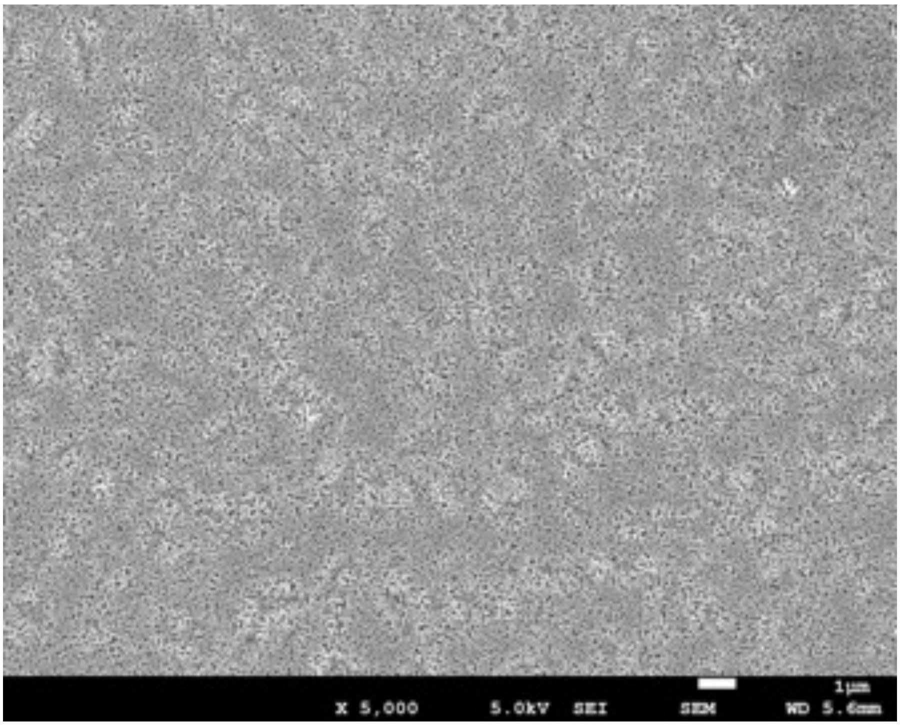

Figure 21.a. Low magnification FESEM images showing top view of SnO_2 nanorods.

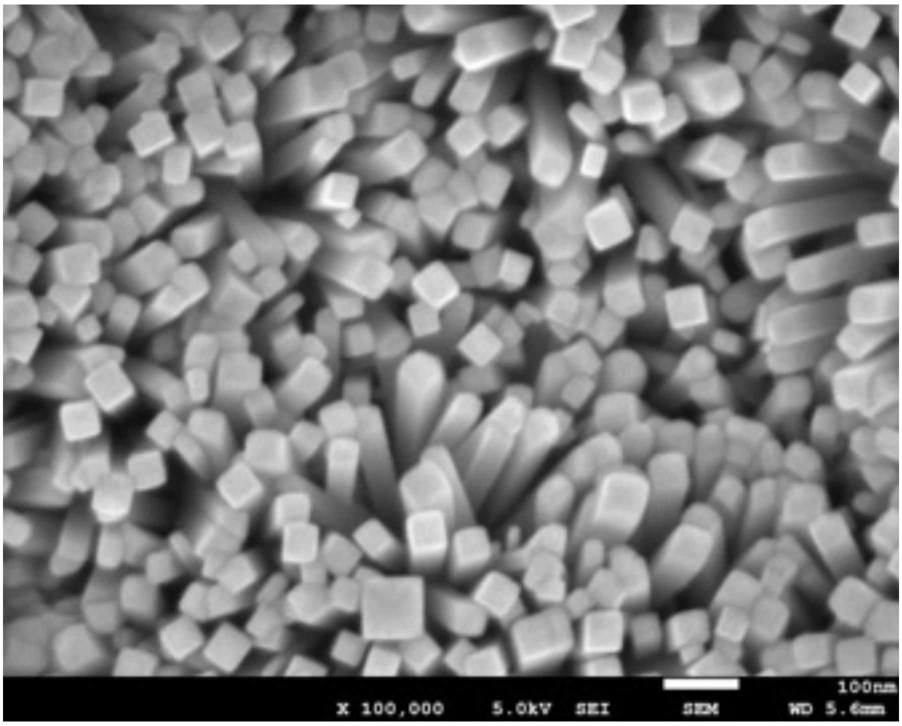

Figure 21.a. High magnification FESEM images showing top view of rectangular SnO_2 nanorods.

Figure 21 shows the typical top-veiw SEM images of SnO_2 nanorods growth. The nanorods with rectangular cross section are highly orderly and large-scale uniformly growth on the FTO substrate. According to the SEM images, it can be seen that each SnO_2 nanorods showing independently existing.

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Chapter 7

Conclusion and Scope for Future Work

The main aim of the research was to synthesize uniform 1D nanorods and its application on the ETL layers of the photovoltaic devices. During my research project, we synthesized as well as optimized the well oriented SnO_2 nanostructure. Here we try to fabricate SnO_2 ETL layer by using hydrothermal process. For fabrication of device, SnO_2 nanorods have been synthesized with ZnO seed layer over TCO substrate. After that Au is coated over the SnO_2 nanorods to increase the the absorbtion. The experiment is carried out in the ambient conditions and the result is the formation of uniform rectangular nanorods.

One dimensional SnO_2 nanostructures can be used for many optoelectronics applications like, Photovoltaic, light emitting diode, and Dye degradation. SnO_2 nanostructure due to its high charge carrier mobility and high diffusion lengths and its advantages over other ETL materials like TiO_2, ZnO is more suitable for solar cell applications. We can fabricate a working prototype of a solar cell with high efficiency just by using a glove box. Au decorated SnO_2 nanorods can be used for solar cells. Au nanoparticles increase the photoelectrons and therefore re- sults in higher current density. Therefore, solar cell fabricated by using Au deco- rated SnO_2 ETL results in higher efficiencies.

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