

In this thesis work, various synthesis processes and characterization techniques have been utilized. This chapter will discuss these synthesis and characterization techniques in detail. Section 4.1 deals with materials' synthesis and solar cell preparation process. Prepared materials and solar cells were characterized further to understand the effect of processing variables. Section 4.2 deals characterization techniques used for understanding the photovoltaic response of the prepared devices in detail.

4.1 Fabrication and Synthesis Techniques

This section will discuss methods adopted for synthesis of quantum dots (QDs), preparation of photoelectrode material and fabrication of solar cells.

4.1.1 Fluorine Doped Tin Oxide (FTO) Substrate Preparation for Photoelectrode Material Deposition

Fluorine doped Tin oxide (FTO) was cleaned and surface of FTO was treated prior to photoelectrode material deposition. These processes are discussed in details in subsequent subsections.

4.1.1.1 FTO Cleaning

FTO substrates were cleaned by ultrasonicing in a soap solution bath for one hour followed by ultrasonic bath in ethanol for one hour. After ultrasonic bath, FTO substrates were rinsed using deionized (DI) water and dried using nitrogen gas. After drying, FTO substrates were stored in vacuum for further use.

4.1.1.2 Titanium Chloride Treatment of FTO

After cleaning, FTO substrates were treated with titanium chloride (TiCl_4) solution for blocking layer deposition. TiCl_4 solution was prepared by preparing 30 mM solution of TiCl_4 in cold DI water. Cleaned FTO substrates were dipped in TiCl_4 solution and heated at 70 °C for 30 minute. After heating, FTO substrates were removed from TiCl_4 solution and calcinated for 30 minute at 450 °C. After calcination, substrates were cooled down naturally to room temperature. Treated FTO substrates were stored under vacuum for further processing.

4.1.2 Photoelectrode Material Preparation and Deposition over Treated FTO Substrate

Zinc titanate nano particles were synthesized using sol-gel technique and TiO_2 anatase nano-particles were purchased from Sigma Aldrich for their use as the photoelectrode materials. A paste of photoelectrode material was prepared and deposited using Dr-blade (i.e. Drag-blade) method on treated FTO substrates. Photoelectrode material preparation and Dr-blade deposition are discussed in the subsequent subsections.

4.1.2.1 Zinc Titanate Photoelectrode Material Preparation

Sol-gel method is adopted for preparation of zinc titanate nano-powder. For a typical synthesis, zinc acetate dihydrate 14 mmol is added in 15 ml of 2-propanol. 14 mmol of ethanolamine is added to the solution of zinc acetate dihydrate and stirred continuously at 60 °C to get a transparent solution. 14 mmol of titanium isopropoxide is added drop by drop in

zinc acetate mixture. 4-5 drop of concentrated nitric acid is added to 40 ml of DI water in a separate beaker and diluted nitric acid is added dropwise to earlier prepared mixture of titanium and zinc precursors. This prepared mixture is stirred continuously at room temperature till gel formation. Prepared gel is dried at 110 °C for four hours and calcinated at different temperature for different duration to get different phases and morphologies of the synthesized materials.

4.1.2.2 Photoelectrode Material Paste Preparation for Deposition over Treated FTO

Photoelectrode material paste was prepared for deposition on treated FTO. For the same, 1 g of ethyl cellulose is added in 20 ml of ethanol and stirred continuously till a homogeneous solution is obtained. This solution is named as ethyl cellulose solution. For a typical paste preparation, 1 g of nano-powder of photoelectrode material (zinc titanate or anatase titanium dioxide) is dissolved in 5 ml of terpene oil and 1 ml of ethyl cellulose solution with 5 ml additional ethanol. This mixture is stirred continuously at 70 °C to achieve desired viscous paste for mesoporous electrode deposition on treated FTO using Dr. blade method.

4.1.2.3 Photoelectrode Paste Deposition over FTO and Mesoporous Electrode Preparation

Scotch tape is used as spacer to deposit photoelectrode material paste over TiCl_4 treated FTO substrates. Paste is poured on FTO substrate after putting scotch tape as spacer. The paste was uniformly distributed by dragging a glass rod over scotch tape on FTO substrate. The paste deposited electrodes are dried at 80 °C for 1 hour and finally calcinated at 500 °C for 2 hours. The prepared mesoporous electrodes are either used directly for fabricating device or kept under vacuum for later use.

4.1.3 QDs Synthesis Techniques, Sensitization of Mesoporous Electrode and Surface Treatment

QDs synthesis and sensitization of mesoporous electrodes have been done using two methods in this work. Section 4.1.3.1 describes in-situ hydrothermal synthesis and sensitization process simultaneously while section 4.1.3.2 describes successive ionic layer adsorption and reaction (SILAR) sensitization process.

4.1.3.1 Hydrothermal Synthesis of QDs and In-Situ Sensitization

Synthesis of QDs can be divided in two parts. One is nucleation and second is growth of QDs. In hydrothermal synthesis, nucleation and initial growth take place first after mixing of cationic and anionic precursors and later on mixture is transferred to autoclave and heating to a certain temperature and duration for desired growth. This work focused on hydrothermal synthesis of cadmium telluride (CdTe) quantum dots.

In a typical synthesis, Cd precursor (Cadmium Chloride) was dissolved in water and 30 mM solution of Cadmium Chloride (CdCl_2) was prepared. N - acetyl cysteine (NAC) was dissolved in water in ratio 2.5:1 (Cd:NAC) along with cadmium chloride. 1 M solution of sodium hydroxide (NaOH) was prepared in water. pH of cadmium precursor solution was adjusted using 1 M NaOH solution in range of 7-11. Cadmium precursor was kept under continuous flow of nitrogen (N_2). A colorless solution was obtained. Tellurium (Te) powder was reduced in water in the presence of sodium borohydride (NaBH_4) reducing agent. Cd:Te molar ratio was adjusted to 2:1. A continuous flow of N_2 was maintained to avoid oxidation of reduced Te solution. A blackish color solution was obtained. Tellurium mixture was also heated at 65 °C until a purple color was obtained indicating formation of sodium hydrogen telluride (NaHTe). NaHTe was injected swiftly into cadmium precursor with the help of a syringe. Immediate nucleation started as color of Cd precursor changed from colorless to yellow. This mixture was quickly transferred to autoclave and heated at different temperature and for

different duration. Figure 4.1 shows a schematic representation of synthesis flow for CdTe quantum dot hydrothermal synthesis.

The mesoporous electrodes were inserted in autoclave consisting of CdTe QDs precursors and sensitization was achieved simultaneously with the growth of CdTe quantum dots to achieve the in-situ sensitization of mesoporous electrodes.

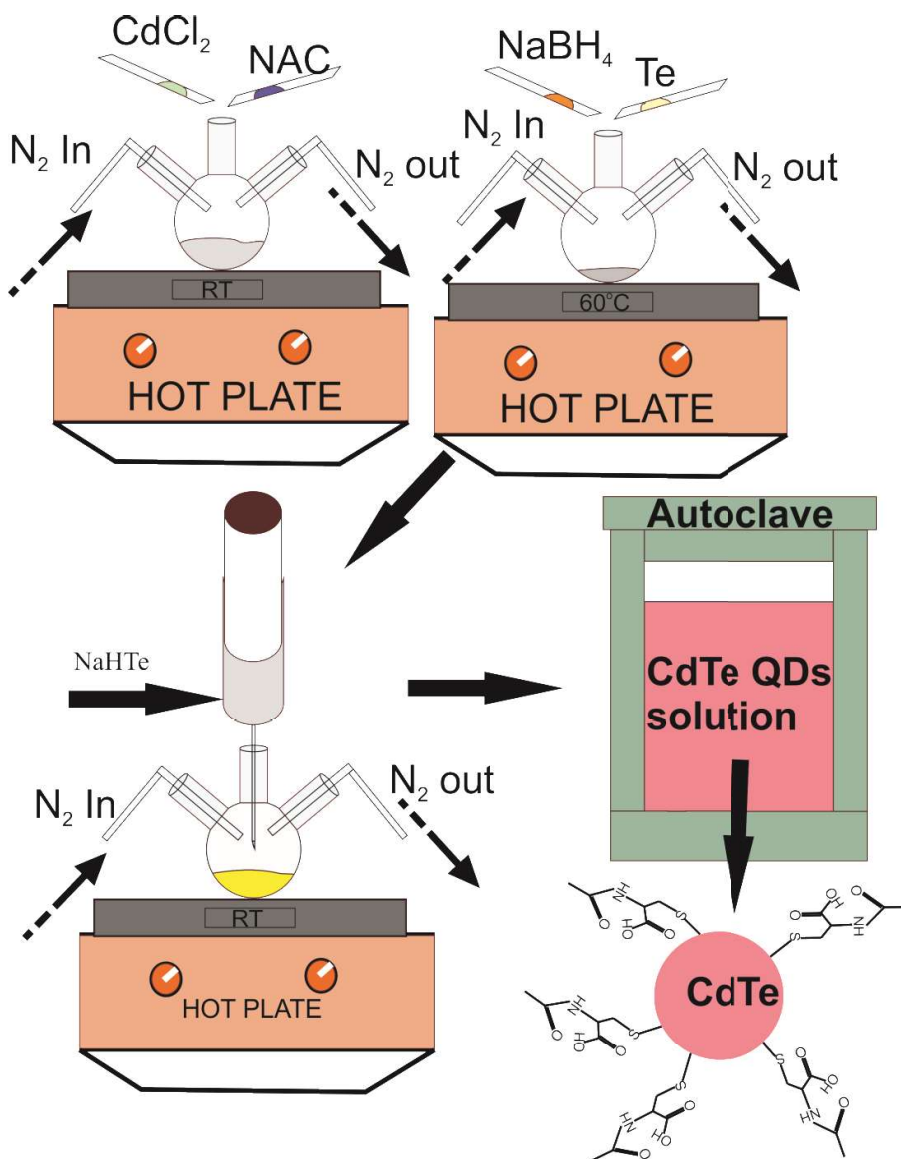


Figure 4.1 Schematic diagram of synthesis of CdTe quantum dots using hydrothermal process and in-situ sensitization of mesoporous electrode using CdTe quantum dots.

4.1.3.2 Successive Ionic Layer Adsorption and Reaction Sensitization

Cadmium sulfide (CdS) quantum dots were adhered over mesoporous electrode using successive ionic layer adsorption and reaction (SILAR) technique. 0.1 M solution of cadmium chloride was prepared in de-ionized (DI) water solvent for cationic solution. 0.1 M solution of sulfur (S) was prepared in DI water to prepare anionic precursor. Mesoporous electrode was

first dipped in cationic precursor for 1 minute and washed by DI water followed by drying using N_2 gas. After that, mesoporous electrode was dipped in anionic precursor for 1 minute followed by washing with DI water and drying by N_2 gas. This is one complete SILAR cycle and 8 such SILAR cycles were repeated for CdS quantum dots sensitization of mesoporous electrode. Higher cycles resulted in agglomeration of quantum dots on top of mesoporous electrode surface only. Figure 4.2 shows the schematic representation of SILAR cycles for CdS sensitization of mesoporous electrode.

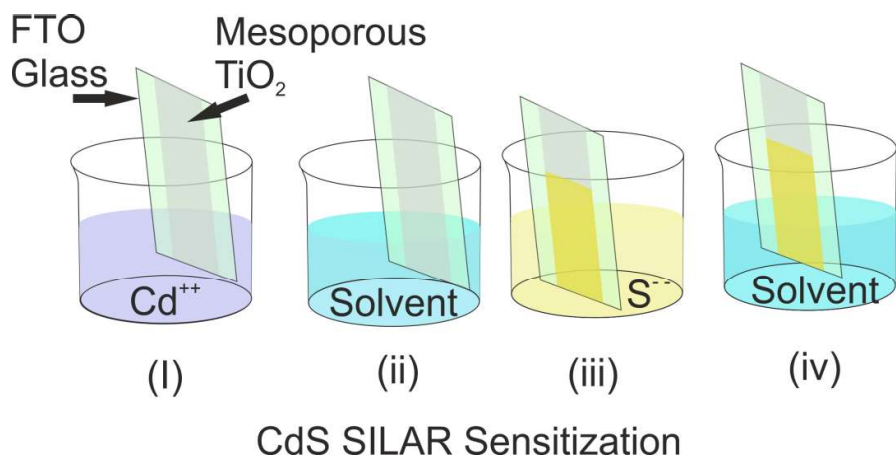


Figure 4.2 CdS quantum dots sensitization of mesoporous electrode using SILAR.

4.1.3.3 ZnS Surface Treatment for Sensitized Mesoporous Electrode

Mesoporous electrodes were passivated with zinc sulfide (ZnS) using SILAR method. 0.1 M zinc precursor was prepared by dissolving zinc acetate in DI water and 0.1 M precursor of S was prepared by dissolving sulfur powder in DI water. The sensitized electrodes were dipped first in Zn precursor solution for 1 minute and then rinsed by DI water. After that sensitized electrodes were dipped in sulfur precursor for 1 minute and rinsed by DI water followed by drying with N_2 stream. This completed one SILAR cycle for ZnS deposition. Three such SILAR cycles were used for ZnS passivation of sensitized electrodes.

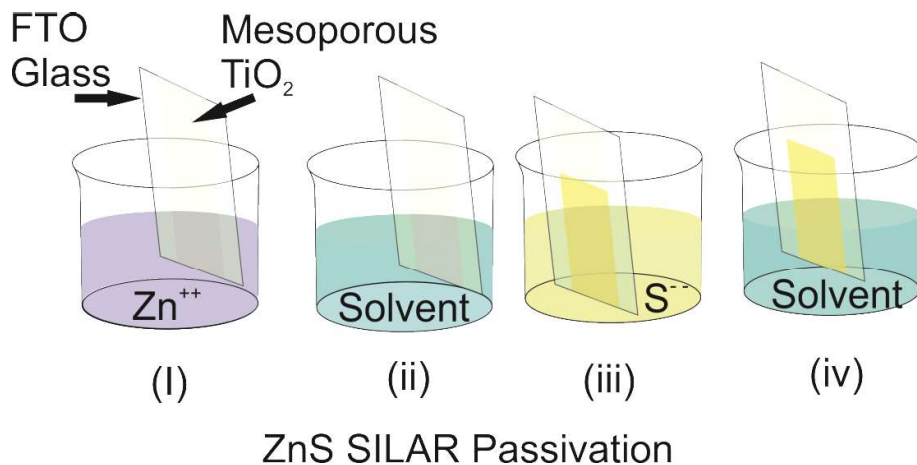


Figure 4.3 ZnS passivation of sensitized mesoporous electrode using SILAR method.

4.1.4 Polysulfide Electrolyte Preparation

Polysulfide electrolyte was prepared by adding 0.78 g (1 M) sodium sulfide (Na_2S), 0.03 g S (1 M) and 0.15 g (0.2 M) potassium chloride (KCl) in 10 ml of DI water. This mixture was stirred continuously till a uniform yellow solution was obtained. This prepared electrolyte was stored under vacuum in dark for further use.

4.1.5 Counter Electrode Preparation

PbS/Pb and Cu_2S /Brass counter electrodes were prepared in this work and discussed in the following subsections.

4.1.5.1 PbS/Pb Counter Electrode Preparation

PbS/Pb counter electrode was prepared by dipping Pb slab in concentrated H_2SO_4 solution for 24 hour. After that, Pb slab was dipped in polysulfide electrolyte for 24 hour. Pb slab was rinsed by DI water and dried using N_2 gas. Prepared PbS/Pb slab was utilized as counter electrode in sandwiched configuration.

4.1.5.2 Cu_2S /Brass Counter Electrode Preparation

Brass sheet was cleaned in ultrasonic bath of soap solution for 30 minute and rinsed by DI water. After that brass sheet was cleaned by ultrasonic bath in ethanol for 30 minute and rinsed by DI water and dried using N_2 stream. To prepare Cu_2S /Brass counter electrode, cleaned brass sheet was dipped in concentrated HCl for 10 minute at 70 °C to etch Zn from top layers of brass followed by rinsing with DI water and drying with N_2 gas. This etched brass sheet was dipped in polysulfide electrolyte for 30 minute to prepare Cu_2S /Brass counter electrode. After dipping in polysulfide electrolyte, sheet was rinsed by DI water and dried using N_2 gas. These prepared counter electrodes were stored in vacuum for further use.

4.1.6 Assembling of Quantum Dot Sensitized Solar Cell (QDSSC)

Assembling of QDSSC was done by sticking counter electrode with passivated sensitized mesoporous electrode using 60 micrometer thick thermoplastic sheet and inserting polysulfide electrode with the vacuum infiltration technique. In another assembling method, counter electrode and passivated sensitized mesoporous electrode were sandwiched using scotch tape as spacer and few drops of polysulfide electrolyte were added over passivated mesoporous sensitized electrode prior to sandwiching.

4.2 Characterization techniques

Various characterization techniques were adopted to achieve the desired properties of QDSSC sub-components and for recording the photovoltaic performance of QDSSC. These characterization techniques can be classified in categories like structural characterization, optical characterization, surface morphology characterization and electrical characterization. These techniques are discussed in details in subsequent subsections.

4.2.1 Structural Characterization and microstructural characterization techniques

For structural characterization of mesoporous electrode, X-ray diffraction technique has been utilized. For microstructural characterization, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) have been utilized. These techniques have been discussed in following subsections.

4.2.1.1 X-ray Diffraction Characterization Technique

X-ray diffraction (XRD) is used to identify crystal structure i.e. crystallographic phase of samples under test. X-ray electromagnetic waves were invented by Wilhelm Conrad Rontgen in 1885 and their wavelength lies in range $0.01 \text{ \AA} - 100 \text{ \AA}$. Further, X-ray diffraction was first observed in 1912 and subsequently used for estimation of crystal structure. X-rays are generated during collision process between metal target and high speed accelerated electrons.

X-ray tube is used to generate X-rays. A high-voltage is applied to accelerate thermally generated electron towards target usually Cu target for generation of $K\alpha_1$ X-ray. A schematic diagram showing generation of characteristic X-ray $K\alpha_1$ is shown in Figure 4.4.

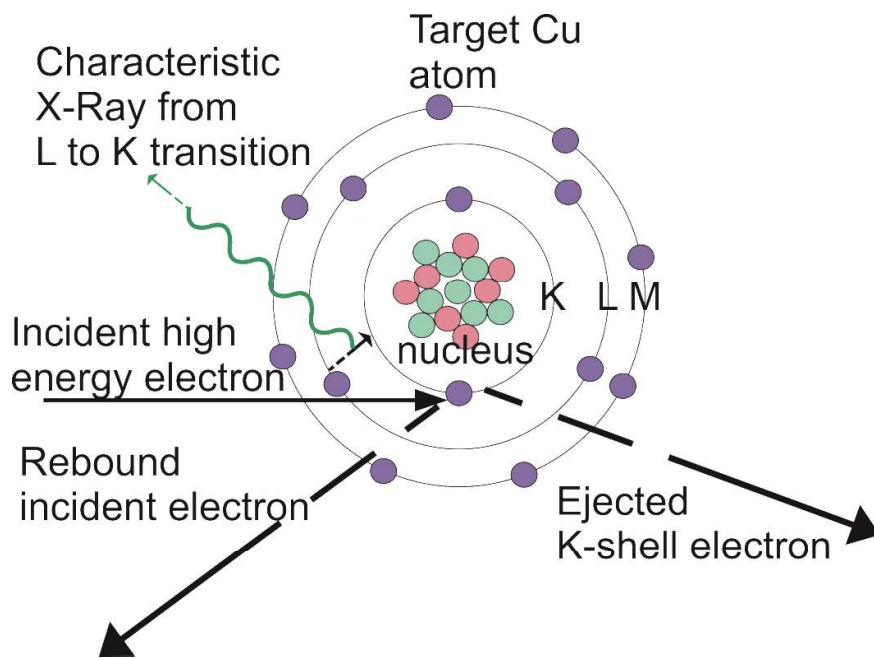


Figure 4.4: Schematic diagram showing generation of characteristic X-ray.

X-ray diffraction is based on interference of diffracted waves. It provides information about interatomic spacing of crystal planes when combined with Bragg's law. A schematic diagram of X-ray diffractometer is shown in Figure 4.5. X-rays are generated first and then passed through a monochromator. After passing through monochromator, $K\alpha_1$ X-rays are only available for diffraction experiments. Then these nearly monochromatic X-rays are passed by anti-divergent slit followed by soller slit to collimate X-rays. After that they are passed through anti-diffusion slit and then allowed to fall on sample.

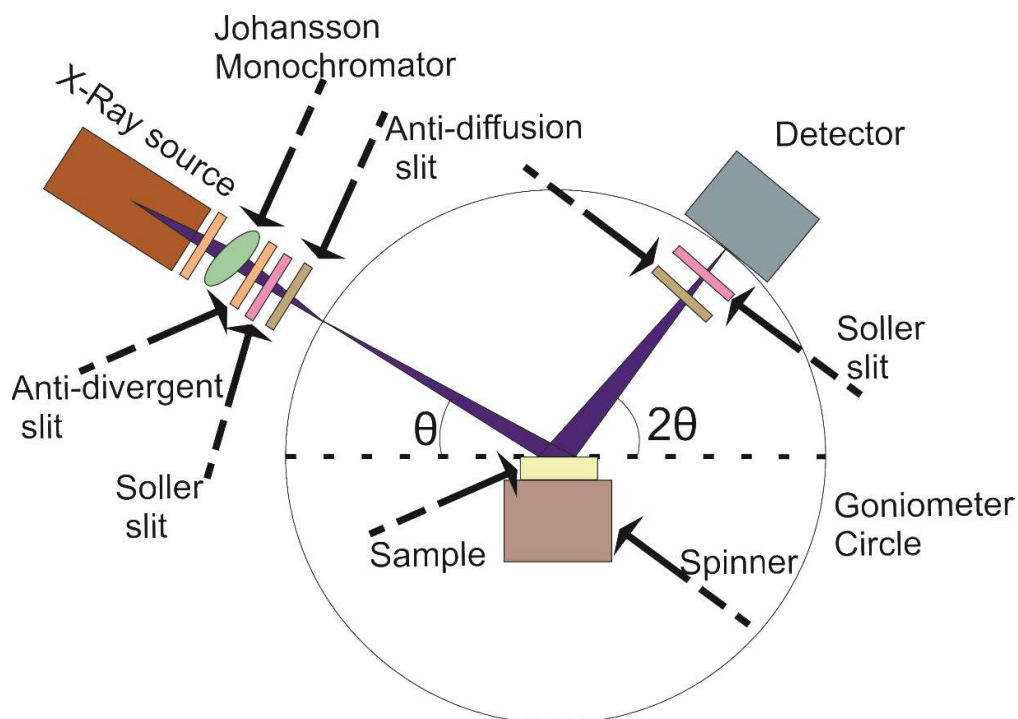


Figure 4.5: Schematic diagram of components of X-ray diffractometer.

Diffracted beam is first passed through anti-diffusion slit followed by Soller slit and collected at detector. The Bragg-Brentano geometry is commonly used geometry for XRD experiments. In this reflection geometry, divergent and diffracted beams are focused at a fixed radius from the sample position. In this work, Bruker D8 advance X-Ray diffractometer along with parallel beam geometry was utilized for recording X-ray diffraction pattern.

4.2.1.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) has been utilized to study surface morphology of mesoporous electrodes and sensitized mesoporous electrodes. The essential components of SEM are shown in a schematic diagram, Figure 4.6. Electron microscopy makes use of electron beam and series of electromagnetic lenses to focus electron beam. Electromagnetic lenses are used to focus electron beam as probing beam and electron beam probe is scanned through sample. Probe scanning/rastering is operated by a beam deflection system, integrated within the objective lens. The deflection system of the electron probe is controlled by a pair of electromagnetic coils or scanning coils. Apertures are controlled to adjust the divergence of the electron beam in its optical equivalent path. The optimal setting of operational parameters is necessary to have desired depth of field and resolution. The depth of focus is strongly affected by the working distance and aperture size. The resolution of an image is adjusted by the accelerating voltage of electron gun and probe current. We have employed Carl Zeiss SEM EVO 18 special edition scanning electron microscopy to study surface morphology of mesoporous electrode before and after sensitization.

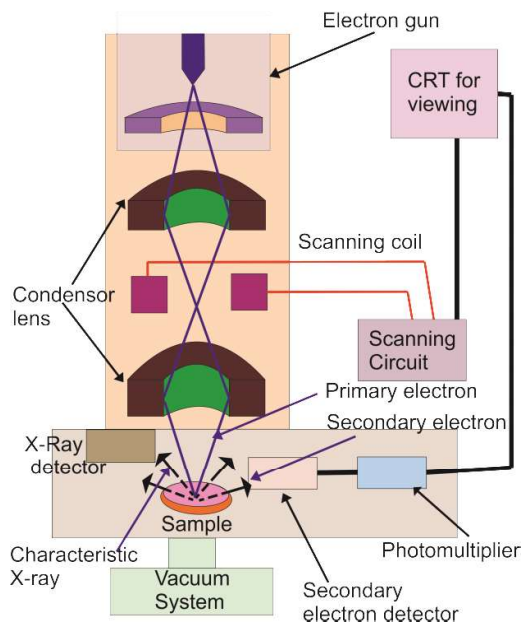


Figure: 4.6 Schematic diagram showing components of scanning electron microscopy.

4.2.1.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is another measurement system in scanning probe microscopy class. AFM utilizes near-field force between atoms of probe tip and surface to generate signal for surface topography. Figure 4.7 shows a schematic diagram of atomic force microscopy. Near field force between the tip and sample is detected using a piezo based scanning head and associated distance between tip and sample is calculated and shown in conjunction with a topography image.

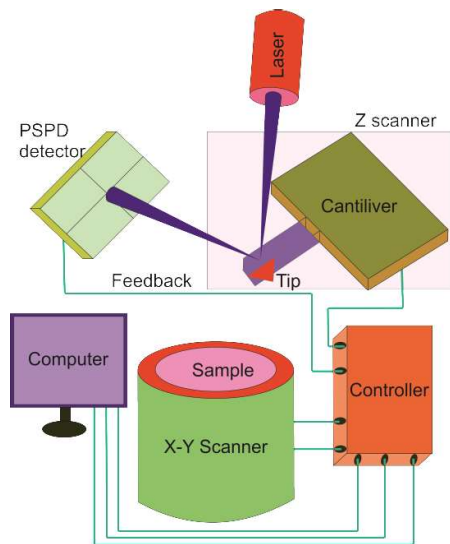


Figure: 4.7 Schematic diagram of atomic force microscopy.

A Park system, scanning probe microscopy XE-70 has been used to estimate surface topography, and surface roughness. AFM topography is collected in non-contact mode for mesoporous electrode and sensitized electrode at different scanning areas. An oscillation frequency is chosen for AFM tip in non-contact mode and slow scan rate was utilized for getting topography information. XEP software provided by Park System was used to collect the topography and XEI software from Park System was used to analyze topographical information for surface roughness. Artifacts were also removed by XEI software during the analysis of AFM micrographs.

4.2.2 Optical Characterization

Optical properties of photoelectrode materials, quantum dots and sensitized electrodes are deciding factor when it comes to dictating the photovoltaic performance of a QDSSC. UV-Vis spectroscopy has been utilized for measuring absorption of quantum dots, UV-Vis combined with Diffuse Reflectance Accessory has been utilized for recording diffuse reflectance of mesoporous electrodes and sensitized mesoporous electrode. Fluorescence spectrometer has been utilized for measuring emission spectra of prepared quantum dots. These characterizing techniques have been discussed in following subsections.

4.2.2.1 Ultraviolet Visible Spectrometer

Agilent Cary 4000 Ultraviolet Visible (UV-Vis) spectrometer is used to collect absorbance of prepared quantum dots that cover the wavelength range from 200 nm to 900 nm. It employs Schwarzschild coupling optics to have the maximum light throughput. It uses a floating aluminium casting and double Littrow monochromator for the minimal noise. An integrating sphere accessory, as an external DRA can be coupled with the main system to get diffused and specular reflectance in 200 nm-900 nm wavelength range. An integrating sphere is the optical device capable of collecting and measuring electromagnetic radiation from an object. This integrating sphere is coated with polytetrafluoroethylene (PTFE), a white diffusive material that is mounted in same detector configuration as the main spectrometer. The reflectivity of PTFE is very high 96 % in 200 nm-900 nm wavelength range and that's why it is used as a reference sample. Figure 4.8 shows a schematic diagram of UV-Vis spectrometer.

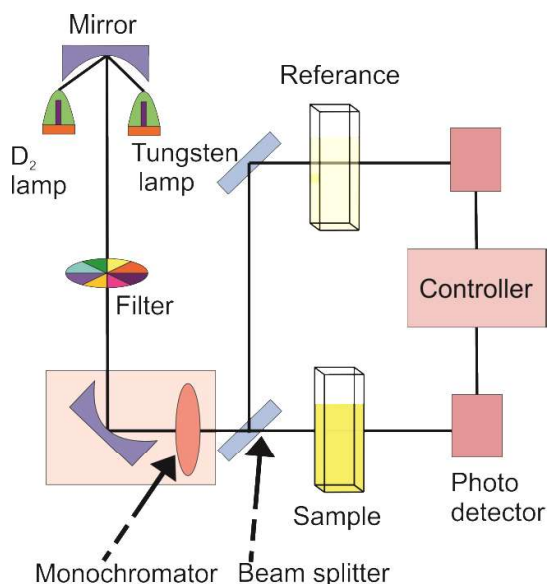


Figure 4.8: Schematic diagram of UV-Vis spectrometer.

The same spectrometer has been utilized to collect absorbance of prepared quantum dots in wavelength range 200 nm-900 nm. Instrument has a photomultiplier tube (PMT) detector. Diffuse reflectance accessory can be attached to the main UV-Vis spectrometer and have option to collect diffuse reflectance and total (diffuse and specular reflectance) reflectance. Using Kubelka Munk transformation, diffuse reflectance can be converted to absorbance in the case of mesoporous electrodes. Prior to collection of diffuse reflectance from mesoporous electrode, a baseline is collected by using a PTFE reference sample.

4.2.2.2 Fourier Transform Infrared Spectrometer

Figure 4.9 shows a schematic diagram of Fourier transform Infrared Spectrometer.

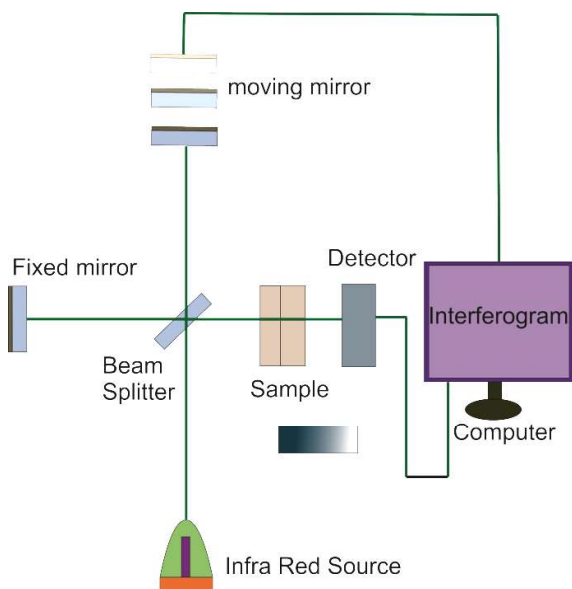


Figure: 4.9 Schematic diagram of FTIR spectrometer.

In this work, a Bruker Fourier Transform Infrared Spectrometer (FTIR) vertex 70v spectrometer is utilized for estimating vibrational spectra. A typical FTIR spectrometer has an Infra-red (IR) source and IR beam is passed through beam splitter towards sample and moving mirror along with towards fixed mirror, Figure 4.9. IR beam interacts with sample and variations in IR beam intensity get recorded at the detector, Figure 4.9. It works on the principle of interaction of infra-red light with vibrating dipole moments of molecule and associated vibrational frequencies with a particular molecule under test can be estimated by examining FT-IR spectrum.

Vertex 70v has an optical bench that can be evacuated to reduce the effect of ambient gaseous molecules for FTIR spectra of sample under test. FTIR spectrometer has a transmittance accessory to hold pallet in disk form and spectrum has been collected in transmittance mode. A sample is prepared in pallet disk for FTIR measurements. First a background spectrum has been collected using a Potassium Bromide (KBr) pallet followed by the sample pallet, made of mixture of sample under test and KBr powder. From these measurements, vibrational bands of sample has been identified and compared with literature for detailed analysis.

4.2.2.3 Fluorescence Spectrometer

Perkin Elmer LS 55 fluorescence spectrometer has been utilized for measuring emission of quantum dots. It makes use of xenon lamp excitation source combined with a monochromator. It has variable width of excitation and emission slits to adjust emission and excitation intensity. Figure 4.10 shows schematic image of fluorescence spectrometer. First, a sample is excited by a fixed wavelength and emission spectrum is scanned over entire range i.e. 200 nm-900 nm. The collected signals at photodetectors are amplified and finally a digitized spectrum is displayed, as explained in Figure 4.10.

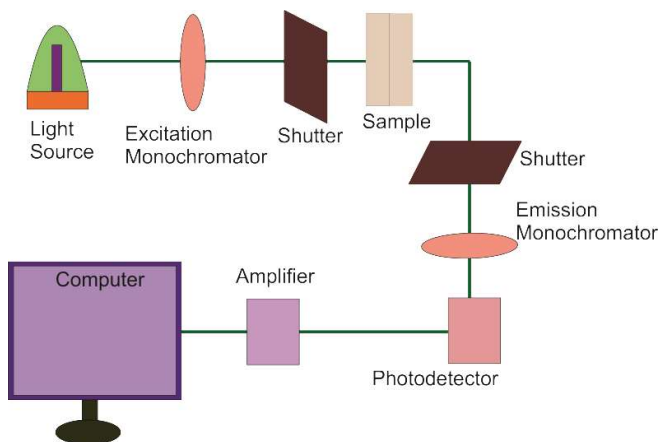


Figure: 4.10 Schematic diagram of fluorescence spectrometer.

4.2.2.4 High Resolution Transmission Electron Spectroscopy

JEOL USA JEM-2100 transmission electron microscope (TEM) has been utilized for imaging the sensitized mesoporous electrode. The JEM-2100Plus (TEM) has a high-stability goniometer stage specifically tuned for high tilt tomographic applications. An X-Y piezo stage is also integrated for sample adjustment. It has three independent condenser lenses and produces the highest electron probe current for given probe size. The improved analytical and diffraction capabilities are possible with such small electron probe. The JEOL Alpha Selector™ allows the selection of a variety of illumination conditions, ranging from full convergent beam to parallel illumination. The standard incorporation of the objective mini lens means that Lorentz microscopy is a standard feature of this microscope. A high contrast aperture is available for any choice of pole piece, allowing high contrast imaging and simultaneous EDS. Figure 4.11 shows a schematic diagram of transmission electron microscopy. An electron gun is utilized as source of high energy electron and anode is used to focus the high energy electron beam. Condenser lens focus the high energy beam on sample. High energy electrons interact with sample and the deflected electron beams are focused on fluorescent screen using electromagnetic objective lens, intermediate lens and projector lens.

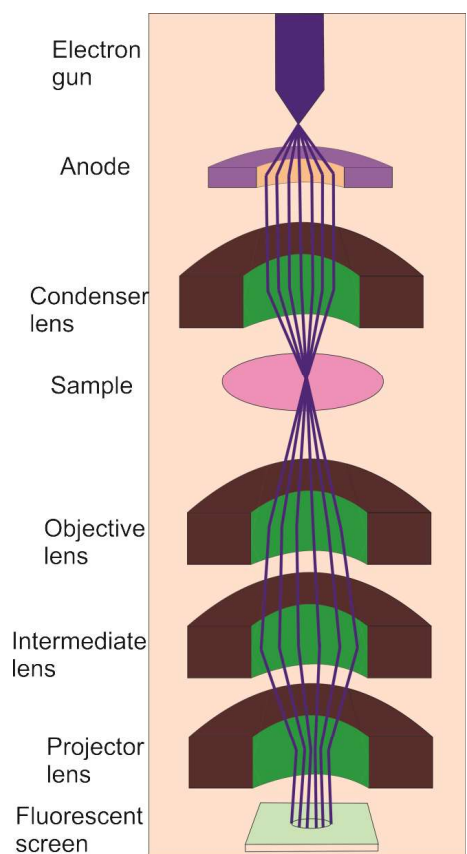


Figure: 4.11 Schematic diagram of transmission electron microscope.

4.2.3 Electrical Characterization

Sensitized mesoporous electrodes have been utilized to prepare Quantum Dot Sensitized Solar Cells (QDSSCs) as discussed in section 4.1.6. These prepared QDSSCs have been characterized for photovoltaic performance. Further, impedance spectroscopy has been utilized to probe the electrical properties of prepared QDSSCs and their correlation with photovoltaic performance. These characterizing techniques have been discussed in brief in subsequent subsections.

4.2.3.1 Photovoltaic Performance Characterization

Photovoltaic performance has been evaluated under 1 Sun illumination using New Port AAA Solar Simulator in Prof. Arie Zaban's lab, Barllan University, Israel. A home built xenon arc lamp based illumination system has been also utilized for producing 1 Sun illumination intensity. Xenon arc lamp illumination was calibrated to 1 Sun intensity using VOLTCRAFT PL-110SM flux meter. Solar cells were tested using New Port AAA Solar Simulator or calibrated xenon arc lamp based illumination system. Current-voltage characteristic was recorded using Autolab Potentiostat PGSTAT302N under simulated AM 1.5 illumination. Photovoltaic performance parameters were extracted from recorded current-voltage characteristic for respective QDSSCs.

4.2.3.2 Impedance Spectroscopy Characterization

Impedance spectroscopy characterization was done using FRA32 module of Autolab Potentiostat 302N. Impedance spectroscopy data was obtained under dark condition at constant dc bias. Impedance spectra were fitted using two models. First model is the transmission line

model and equivalent circuit diagram is shown in Figure 4.12 (a). Here, R_s is a series resistance due the electrical contacts at FTO. B_2 is transmission line element named after Prof. Juan Bisquert and available in NOVA software. B_2 represents a continuous interpenetrating network of mesoporous electrode and polysulfide electrolyte. It consists of combination of resistances and constant phase elements. Some of the variables of element B are fixed and shown in Figure 4.12 (a). Q represents constant phase element (CPE), n represent parameter associated with constant phase element and L represent length of transmission line network. R_1 is designated as R_{tr} . R_{tr} is transmission resistance originating from resistance felt by photo injected electron in mesoporous TiO_2 network. R_3 is designated as R_{rec} . R_{rec} is the recombination resistance indicative of recombination process between photo injected electrons in electron transport material and polysulfide electrolyte. Q_3 is designated as C_{rec} . C_{rec} is chemical capacitance of carriers at electron transport material and polysulfide interface. The interface at polysulfide electrolyte and counter electrode is represented by R_{ce} and CPE_4 , where R_{ce} represents a resistance felt for hole capture at counter electrode and CPE_4 represents a capacitance at counter electrode and polysulfide electrolyte interface. Figure 4.12 (b) shows a simplified model reported by Bisquert et al. in 2009. Here, R_s is again a series resistance as explained earlier. Transmission line is replaced by parallel combination of the recombination resistance R_{rec} and chemical capacitance CPE_1 , while interface between counter electrode and polysulfide electrolyte is represented by R_{ce} and CPE_2 . Transmission line model is used for fitting when transmission line feature is present at respective biased potential in impedance spectra. However, at higher biased potential, the transmission line feature disappears and this simplified model, Figure 4.12 (b) is used for fitting impedance spectra.

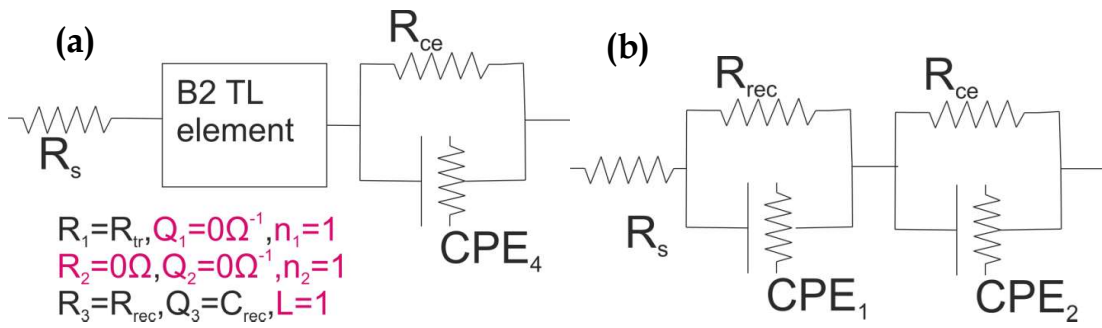


Figure: 4.12 Equivalent circuit models to fit impedance data (a) Transmission line model and (b) Simplified model

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