Chapter 2

Experimental Techniques
This chapter deals with the synthesis and characterization of the NCs and basic details of the experimental techniques utilized to carry out the thesis work with special emphasis on the ultrafast TA spectroscopy. For synthesis of the colloidal NCs high temperature hot injection method was used, the mechanism of which has been described in the Introduction chapter. The size, shape and crystallinity of the NCs were determined through transmission electron microscopy (TEM). Energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) revealed the composition of the NCs whereas X-ray diffraction (XRD) was utilized to determine the crystal structure of the NCs. The steady state optical properties of the synthesized NCs were investigated using UV-vis absorption, photo-luminescence (PL) spectroscopy and excitation spectroscopy. The PL lifetime in nanosecond time-scale was determined from time correlated single photon counting (TCSPC) technique. To investigate the charge carrier dynamics with femtosecond resolution ultrafast TA spectroscopy was utilized. The surface topography of the TiO$_2$ nanoparticulate photoanodes were determined through atomic force microscopy (AFM). To determine the power conversion efficiency (PCE) of the solar cell devices Current density-voltage (J-V) and incident photon to current conversion efficiency (IPCE) measurements were carried out. Electrochemical impedance spectroscopy (EIS) was performed on the solar cell devices to understand the different interfacial recombination processes.

2.1. Synthesis of the Semiconducting Nanocrystals

2.1.1. Materials

Cadmium oxide (CdO, 99.5%), cadmium acetate, dihydrate (CdAc$_2$, 2H$_2$O, 98%), cadmium nitrate tetrahydrate (Cd(NO$_3$)$_2$, 4H$_2$O), lead acetate trihydrate (PbAc$_2$, 3H$_2$O 99.9%), zinc acetate (ZnAc$_2$, 99.9%), gold chloride (98%), sulfur powder (S, 99.99 %), selenium powder (Se, 99.99 %), tellurium tellur (Te, 99.99%), stearic acid (SA, 95%), dodecylamine (DDA, Aldrich), dodecanethiol (DDT, >98%), didodecylammonium bromide (DDAB, Aldrich), sodium sulfide (Na$_2$S), potassium chloride (KCl), potassium hydroxide (KOH), mercaptopropionic acid (MPA), oleic acid (90%), tri-octyl phosphine (TOP, 90%) and octadecene (ODE) (90%) was purchased from Sigma-Aldrich and used.
without further purification. Copper chloride dihydrate (CuCl₂·2H₂O, 99%) and tetrabutylammonium hydroxide pentahydrate (TMAH, 98%) were purchased from Alfa Aesar. In order to clean the NCs AR grade chloroform and methanol were used. Spectroscopic grade chloroform was used for TA measurements. Tetrabutyl-ammonium-perchlorate (TBAP), DCM, and Ferrocene were purchased from Sigma-Aldrich for CV measurements. De-ionized (DI) water was used for phase transfer and electrolyte preparation. TiO₂ transparent (DSL 18NR-T) and scattering (WER2-O) were obtained from Dyesol. For plasma treatment high purity Ar gas was obtained from Six Sigma Gases India Pvt Ltd. (2 ppm moisture, 2 ppm O₂).

2.1.2. Synthesis of CdTe Core and CdTe/ZnS Core/Shell Nanocrystals

CdTe NCs of diameter ~4.6 nm were synthesized according to synthetic methodology reported by Peng et.al. In brief, a mixture of 2 mmol of CdO, 8 mmol of oleic acid and 8 ml of 1-octadecene (ODE) was heated to 260°C under nitrogen to form colorless cadmium oleate. 1 mmol of Te dissolved in TOP and ODE was then injected swiftly to the reaction mixture. The NCs were grown at 240°C. When desired size was reached, the reaction mixture was cooled down and quenched with chloroform. The NCs were precipitated with methanol from chloroform solution for three times. Finally, the CdTe NCs were re-dispersed in chloroform for further experimentation.

ZnS shell was synthesized on top of CdTe core using successive ionic layer adsorption and reaction (SILAR) method following previous literature with few modifications. At first, Zn-oleate solution of desired amount was prepared by dissolving Zinc acetate tetrahydrate in oleic acid and ODE at 180°C. Similarly, sulfur was dissolved in TOP and ODE to prepare S-TOP. The CdTe NCs dispersed in ODE were heated to the 220°C for shell growth. Required amount of the Zn-oleate solution and S-TOP solution for 1 ML shell growth were alternatively injected to the NC solution. After each injection the solution was allowed to grow for 10 minutes. When desired shell thickness is reached, the reaction mixture was cooled down and the NCs were cleaned using the same procedure for CdTe core.
2.1.3. Synthesis CdTe/ZnSe Core/Shell Nanocrystals

The CdTe/ZnSe core/shell NCs were synthesized at different reaction temperatures using the CdTe core using standard successive ionic layer adsorption and reaction (SILAR) technique. Briefly, amount of Zn and Se precursor were calculated from the concentration of the CdTe core for the desired shell thickness. Required amount of Zn acetate terahydrate was dissolved in 4 equivalent of oleic acid at 180°C and used as Zn-precursor. TOP-Se solution in ODE was used as Se-precursor. The CdTe NCs in ODE was heated to desired temperature followed by alternate addition of Zn-oleate and Se-TOP in the interval of at least 10 minutes. The precursors were added dropwise to ensure complete adsorption on CdTe surface. The cleaning procedure for the core/shell NCs were same as the CdTe core. The core/shell CdTe/ZnSe NCs with 1ML of shell thickness were synthesized at nominal 220°C shelling temperature (CdTe/ZnSe)_220 and at high ~280°C shelling temperature (CdTe/ZnSe)_280. Three core/shell NCs were synthesized where sequential heating/cooling at different temperatures were performed. For (CdTe/ZnSe)_21 Zn-oleate was injected at 220°C and then the temperature was raised to 280°C, kept for 10 minutes and again cooled to 220°C for Se injection. After Se injection the NCs were grown for 10 minutes. Then the temperature was increased to 280°C without purification and the solution was kept for 20 minutes for (CdTe/ZnSe)_22. For (CdTe/ZnSe)_23 1.5ML of shell was grown on top of CdTe core where the aforementioned sequential temperature change protocol was used similar to (CdTe/ZnSe)_21.

2.1.4. Synthetic procedure for CdSe/PbSe Janus Hetero-Nanocrystals

For all the synthesis metal: Se was kept 2:1 unless otherwise stated. For pure CdSe (A series) synthesis 2 mmol (0.256 gm) CdO, 8 mmol OA (2.5mL) and ~8mL ODE was heated ~ 250°C in a three necked flask under nitrogen atmosphere to obtain a clear solution. At this temperature, Se-TOP (1mmol) dissolved in 2mL ODE was swiftly injected to the reaction flask and the NCs were grown at ~270°C. Aliquot were taken out at regular time intervals and quenched with chloroform followed by precipitating thrice using methanol. The NCs were then re-dispersed in chloroform for optical studies. For NCs with Pb, a mixture of CdO and PbAc2, 3H2O (molar ratio varied from series B to D) were taken keeping all other conditions the same. The molar ratio between CdO and
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PbAc2, 3H2O was varied as follows: 90:10 (B series), 75:25 (C series) and 50:50 (D series). For example in D series, 1 mmol of CdO and 1 mmol of PbAc2, 3H2O (therefore the total amount of cationic precursor is 2 mmol), 8 mmol OA (2.5mL) and ~8mL ODE was taken and at ~250°C under nitrogen Se-TOP (1mmol) dissolved in 2mL ODE was swiftly injected to the reaction flask and the NCs were grown at ~270°C.

2.1.5 Synthesis of Cu-doped CdSe Nanocrystals

Cu-doped CdSe NCs have been synthesized using synthetic method reported in literature with required modifications. At first, Cu-stearate was synthesized from CuCl2 and SA following procedures of Srivastava et. al. Briefly, 5ml 2.9 gm of 25% methanolic TMAH solution was added dropwise to 10mmol SA dissolved in 20 ml methanol at 50°C while stirring. After 30 minutes 4mmol of CuCl2 in 10 ml methanol was dropwise added to the solution. The resulting sky-blue precipitate of copper stearate (Cu-SA) was separated, washed with methanol dried under vacuum. In a typical synthesis of Cu-doped CdSe NCs, 1 mmol of CdAc2, 2H2O, 0.1 mmol of Cu-SA (mole ratio 1:10), 4 mmol of OA was heated to 180°C in 10 ml ODE under nitrogen atmosphere. At 180°C 0.25 mmol of Se-TOP in 1ml ODE was rapidly injected into reaction mixture. The reaction was continued for 20 minutes at 170°C to ensure incorporation of Cu. In this method the Cu-precursor remains present when the NCs nucleate in the solution leading to incorporation of Cu within the NC. Once the reaction was complete the NCs were washed with methanol thrice to remove all the excess precursors and re-dispersed in chloroform. The temperature was maintained at 170°C as black CuSe formed at higher temperatures. The Cu-precursor (Cu-SA) is a Cu^{2+} complex, but TOP can reduce Cu^{2+} to Cu^{+} under inert N2 atmosphere during the synthesis.

2.1.6 Synthesis of Alloy Nanocrystals.

For CdSe NC synthesis 1 mmol (0.256 g) CdO, 4 mmol OA (2.5 mL), and ~8 mL of ODE were heated at ~250 °C in a three necked flask under nitrogen atmosphere to obtain a clear solution. At this temperature, Se-TOP (0.5 mmol) dissolved in 2 mL of ODE was swiftly injected to the reaction flask, and the NCs were grown at ~250 °C until the desired size was reached. For CdSSe NCs Cd: chalcogen ratio was kept same and
a mixture of chalcogen was taken (for example Se: S = 3:7) in TOP and injected ~ 250°C to the Cd-oleate solution and the growth was continued ~ 230°C to promote graded structure formation. To synthesize CdZnS and CdZnSe NCs similar procedure was followed. The metal precursors of CdO (1.5 mmol) and ZnAc₂ (0.5 mmol) were taken in a three-neck round bottom flask. To this 2.5 ml of oleic acid and 8 ml of the ODE were added. The solution was the heated upto 300°C under inert condition. A chalcogenide mixture of 1 mmol Se, 0.5 ml TOP and 2 ml of ODE was injected swiftly in the solution 300°C. The solution was then maintained at 280°C for 10 minutes to allow the NC to grow. The solution so formed was washed with methanol and then redispersed in chloroform. For synthesis of CdZnS NCs in the chalcogenide mixture instead of Se, S was taken.

2.1.7. Synthesis of Au-CdSe/PbSe HNCs.

To synthesize Au-CdSe/PbSe heterostructures following procedures reported previously by Mokari et al. with required modifications. 0.1 mmol of Gold chloride (AuCl₃), ~1 mmol of DDA and 0.2 mmol of DDAB were dissolved in 8 mL of toluene under N₂ atmosphere. The presynthesized CdSe/PbSe NCs (~25mg) were dissolved in 5 ml of toluene under N₂ to which the gold precursor was added dropwise at room temperature under stirring. The solution was kept for 20 minutes followed by precipitating with methanol. After cleaning twice the NCs were redissolved in chloroform. To grow small Au NPs on CdSe/PbSe surface half of the gold precursor was used keeping other conditions the same.

2.2. Characterization of the NCs

2.2.1. Absorption, Photoluminescence and Excitation Spectroscopy

Ultraviolet-Visible (UV-Vis) Absorption Spectroscopy is informative about the electronic transitions present within the sample. Here, intensity of the incident light (Iₒ) and transmitted light (I) is measured and absorbance (\(A = \log(I/I_o)\)) vs. wavelength (\(\lambda\)) is plotted. According to Beer-Lambert law for reasonably dilute solution

\[ A = \varepsilon_c cl \]
Where $\varepsilon$ is the molar extinction coefficient (cm$^{-1}$M$^{-1}$), $c$ is the sample concentration (M) and $l$ is the path length (1 cm). The NC size can be estimated from the absorption maxima as for larger size the first excitonic maxima red shifts. Moreover, the sharp first excitonic maxima is indicative of good size distribution.

After photo-excitation the sample can emit photons which are detected through photo-luminescence spectroscopy. In PL spectroscopy Xe lamp is used as an excitation source and the excitation light is sent through a monochromator to select the excitation wavelength (Figure 2.1). The emitted photons are collected at perpendicular angle and detected by PMT. The band-edge emission for semiconducting NCs (discussed in detail in chapter 1) is a characteristic property and thus PL spectroscopy provides valuable information about sample quality and purity. It also provides information about interaction of two different molecules through quenching experiments. On the other hand, detecting at a fixed emission maxima and varying the excitation wavelength on the sample excitation spectra can be obtained. From the excitation spectra the optical transitions responsible for emission at a particular wavelength can be identified. PLQY of the NCs were measured with the following equation using rodhamine6G as reference:\(^\text{12}\)

$$Q_{\text{NC}} = \frac{Q_{\text{Ref}}}{\eta_{\text{Ref}}} \frac{PL_{\text{NC}}}{PL_{\text{Ref}}} \frac{Abs_{\text{Ref}}}{Abs_{\text{NC}}} \frac{\eta_{\text{NC}}}{\eta_{\text{Ref}}}$$  \hspace{1cm} (2.23)

Where, PL is the area under the emission curve, Abs is the absorbance at excitation wavelength and $\eta$ is the refractive index of the solvent.

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Figure 2.1. Schematic Layout of (a) Absorption spectrometer and (b) Photoluminescence spectrophotometer.
In this thesis, the UV-vis absorption spectra were recorded on a JASCO-640 spectrophotometer whereas the photo-luminescence spectra and excitation spectra were recorded using Hitachi-4010 spectrofluorometer with detection range 250-850 nm.

2.2.2. Transmission Electron Microscopy (TEM)

Microscope, by definition is a tool that can resolve beyond 0.1 mm (resolution of human eye is ~ 0.1-0.2 mm). The resolving power \( d \) of optical microscope is given by Rayleigh formula as:

\[
d \approx \frac{\lambda}{2 \text{ (N.A.)}} \tag{2.24}
\]

Where \( \lambda \) is the wavelength of light, N.A. is the objective numerical aperture. Considering N.A. of 0.95 the resolution with 600 nm light is around 315 nm which is not sufficient for nanomaterials having size in the order of nm. This limitation can be overcome in Transmission electron microscope (TEM) where high energy electrons are used for imaging instead of light. The wavelength of an electron is given by de Broglie equation as

\[
\lambda = \frac{h}{p} \tag{2.25}
\]

Where \( h \) is the Planck’s constant and \( p \) is the momentum. Under high voltage \( E \) electron of mass \( m_0 \) attains momentum

\[
p = \sqrt{2Em_0} \tag{2.26}
\]

So that \( \lambda \) (in nm unit) can be expressed as

\[
\lambda = \frac{h}{\sqrt{2Em_0}} \approx \frac{1.22}{E^{1/2}} \tag{2.27}
\]

The accelerating energy utilized in TEM is 100 - 300 KeV and under this high voltage we need to consider the relativistic effects so that

\[
\lambda = \frac{h}{\sqrt{2Em_0(1 + \frac{E}{2m_0c^2})}} \tag{2.28}
\]
For 100KeV energy $\lambda \approx 0.004$ nm, which signifies atomic level resolution is possible with TEM.\textsuperscript{13}

The TEM instrument for which the basic layout is shown in Figure 2.2, consists of illumination system (consisting electron gun and condenser lenses), objective lens and sample holder and imaging system.\textsuperscript{13,14} The electron gun generates the high energy electrons which is transferred to the sample through condenser lenses either in parallel beam mode (used in basic TEM and selected area diffraction) or in focused beam mode (used in scanning TEM). The objective lens collects the electron from that exit from the sample to generate a diffraction pattern in the back focal plane and an image in the image plane. The imaging system consists of several lenses which magnify the image and focus on a viewing screen. In TEM electromagnetic lenses are mostly used to deflect the electrons and all the components are kept under high vacuum.

**Figure 2.2.** Outline of TEM Instrument Showing the Basic Components.
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The phase and crystal structure of the sample can be obtained through selected area electron diffraction (SAED) where diffraction pattern of the sample is recorded. For polycrystalline materials concentric diffraction rings whereas for crystalline materials bright spot pattern are observed. Quantitative analysis of the elements present in the sample and their relative percentage can be obtained through energy dispersive X-ray spectroscopy (EDS) alongside TEM measurements. As the high energy electron beam impinges on the sample surface core electrons gets ejected from the constituting atoms. The resulting vacancies are filled by electrons from higher energy state through emission of X-rays characteristic of the elements present in the sample. The relative intensity of emitted X-rays is plotted vs. energy. Quantitative analysis was performed from the peak intensities compared to a standard sample.

The high resolution-TEM (HRTEM) measurements were carried out in JEOL-JEM-2010 UHR instrument (200 kV) with resolution of ~0.2 nm. The NCs dispersed in chloroform were dropcasted on TEM grids (200 mesh size, holey carbon coated Cu Grid) for imaging. Thus from TEM we can obtain NC morphology (size and shape), elemental composition and crystal phase.

2.2.3. X-ray Diffraction (XRD)

X-ray diffraction (XRD)\(^\text{15}\) is an important technique to determine the crystalline phase and lattice parameters of the NC material. In XRD X-ray beam gets diffracted from the lattice planes of the sample at different angles based on the Bragg’s law

\[
n\lambda = 2d\sin\theta
\]  

(2.29)

Figure 2.3. Basic layout of powder X-ray diffractometer.
Where, \( n \) is the order of diffraction, \( \lambda \) is the wavelength of incident beam (here X-ray), \( d \) is the lattice spacing of the crystal and \( \theta \) is the diffraction angle. Due to diffraction of X-rays from atoms present in the NC a diffraction pattern is generated which provides the information about the periodic arrangement of atoms in NC lattice. Also, the intensity of the diffracted peaks depends on the scattering factor and miller indices of the planes. The scattering factor depends on electron density and increases with increasing the electron density. The size of the NCs can also be determined from the width of the XRD peaks using the Scherrer's formula:

\[
d = \frac{K\lambda}{\beta \cos \theta}
\]  

(2.30)

Where, \( d \) is NC size in Å, \( K \) is the shape factor (close to 1), \( \beta \) is fwhm of the peak and \( \theta \) is the diffraction angle. The basic layout of the powder XRD instrument is shown in Figure 2.3 which consists of x-ray source, sample holder and X-ray detector. During measurement the sample can be kept fixed and the X-ray source and detector rotates or the X-ray source is kept fixed and the sample along with detector rotates.

In this thesis the XRD were recorded using Rigaku Ultima IV X-ray Diffractometer with Cuk\(_a\) source and scintillation counter detector. The X-ray was passed through nickel filter to get monochromatic wavelength. (\( \lambda = 1.54\text{Å}, 40 \text{kV and } 40 \text{ mA} \)). The samples were prepared either in powder form or as a thin film on glass substrate. To obtain the crystal structure the XRD pattern was compared to the standard database of Joint Committee on Powder Diffraction Standards (JCPDS)/ International Centre for Diffraction Data (ICDD).

2.2.4. X-ray Photo-electron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS)\(^{16,17} \) is utilized to determine surface composition and oxidation state of the elements present. In XPS soft-X-rays either Mg K\(_a\) (\( h\nu =1253.6 \text{ eV} \)) or Al K\(_a\) (\( h\nu =1486.6 \text{ eV} \)) impinge on the sample resulting core electrons to eject. The kinetic energy (KE) of the ejected electrons depends on the binding energy (BE) of the electron and spectrometer work function (\( \Phi \)) following the photo-electric effect:
By measuring the KE, the BE of electron can be determined. The BE will depend on the nature of the orbital from which the electron gets ejected and the element itself. The p, d and f orbitals split into $p_{1/2}$ and $p_{3/2}$; $d_{3/2}$ and $d_{5/2}$; $f_{5/2}$ and $f_{7/2}$ levels, respectively due to spin orbit coupling with intensity ratio 1:2; 2:3 and 3:4, respectively. Figure 2.4 outlines the XPS instrument and BE of different electronic levels. Upon X-ray excitation the ejected electrons have to pass between a pair of charged hemispherical plates acting as energy filters which allows electrons of particular KE to pass (known as pass energy $E_{\text{pass}}$). The electron multiplier measures the electron current which is proportional to the number of ejected electrons with that particular KE. $E_{\text{pass}}$ is varied by changing the voltage ($V_R$) on the analyzer generating a plot of counts (number of ejected electrons) vs. KE (or BE by equation 2.31).

The XPS experiments reported in this thesis were carried out in SPECS instrument with monochromatic Al $K_{\alpha}$ excitation source and PHOBIOS 100/150 Delay Line Detector setup. The CIS peak (284.6 eV) coming from adventitious carbon was taken as internal standard and all other peaks were corrected with respect to this. The data was analyzed in CASA-XPS software performing Shirley background correction, Gaussian-Lorentzian deconvolution and quantitative analysis. For QDs the XPS was taken by making a thin film of the QDs on ITO coated glass.
2.2.5. Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM)\textsuperscript{14} has been utilized to determine the surface morphology, elemental analysis (through energy dispersive X-ray, EDS) and device cross sections. For SEM measurements Quanta FEG450 was used with 10KV accelerating voltage. The basic principle of SEM is based on the detection of secondary electrons that are emitted from the sample surface upon electron beam irradiation. The number of secondary electrons depends on the nature of sample and provides the brightness of the image. The incident electron probe is scanned horizontally in two perpendicular directions over sample surface (raster scanning). To obtain the surface morphology of the sample the electron beam scan on the surface is synchronized with the scan in the display unit. The resolution is lower in SEM compared to TEM due to use of low accelerating voltage.

2.2.6. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM)\textsuperscript{18} is an example of scanning probe microscopy (SPM) which can image the topography of non-conductive surfaces with atomic level resolution. In AFM a probe which is a cantilever with a sharp tip (~10 nm) scans over the sample surface. A laser beam is reflected from the cantilever and detected by a position sensitive photo-diode (PSPD). As the tip is brought closer to the sample surface the attractive forces (van der Waals forces) cause the cantilever to bend towards the surface; however if the tip is brought nearer the repulsive force (exchange forces due to overlap of atomic orbitals) start to deflect the tip from the surface. The deflection of the tip causes the laser beam to deflect which is tracked by the PSPD and finally processed by the computer to form an image of the surface. The basic components of AFM are shown in Figure 2.5. AFM can be operated in the contact mode, tapping mode or non-contact mode. In contact mode the deflection of the tip is kept constant using a feedback loop while scanning the surface however, it can cause sample damage. In the non-contact mode the tip is oscillated at the resonant frequency, the amplitude of which is kept constant during scanning. The tapping mode represents an intermediate situation where the tip frequently and softly touches the surface. This mode gives better resolution with
minimal sample damage. In our case we have used the Bruker Multimode 8 AFM in ScanAsyst mode which is automated peak-force tapping method.

In conductive-AFM (c-AFM) simultaneous topography and surface current images are measured. The current-voltage (I-V) curve at a particular location of the sample can also be recorded. In c-AFM current can be detected in the pA range providing electrical characterization of the sample surface. The c-AFM is performed under a bias voltage between the conducting tip and the sample surface and the tunneling current is measured to obtain the current image. The topography is obtained in a similar fashion by measuring the deflection of the tip.

![AFM Instrument Diagram](image)

**Figure 2.5.** Representative Diagram of AFM instrument.

### 2.2.7. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

The mole fractions of Cd and Cu in the system was determined in chapter 5 by inductively coupled plasma time-of-flight mass spectrometer (ICP-TOF-MS, model: Optimass 8000R from GBC, Australia). A 0.1 mL aliquot of the system was first oxidized by a mixture of HNO₃ and HClO₄ mixture and then made up into a known volume with milliQ water for ICP-TOF-MS analysis.
2.2.8. Electron Paramagnetic Resonance (EPR) Spectroscopy

To detect the presence of paramagnetic Cu$^{2+}$ ions in Cu-doped CdSe (chapter 5) electron paramagnetic resonance spectroscopy was carried out in 9.5 GHz Bruker ESP-300 spectrometer (X-band frequency).

2.2.9. Raman Spectroscopy

To characterize the phase of cation exchanged CuS layer (chapter 6) Raman spectra were recorded before and after the cation exchange process using RENISHAW invia-312c23 with 532 nm laser source.

2.3. Techniques to Monitor Ultrafast Processes in Semiconducting NCs

2.3.1. Time Correlated Single Photon Counting (TCSPC)

Time correlated single photon counting (TCSPC)\textsuperscript{12} has been used to measure the PL lifetime of the NC samples in nanosecond time-scale with time resolution of \(~70\, \text{ps}\). The TCSPC setup is from IBH (U.K.) where the NCs were excited with 445 nm pulsed excitation from a laser diode (\(~70\, \text{ps fwhm},\, 1\text{MHz repetition rate}\) and TBX4 detection module (IBH) along with Hamamatsu photo-multiplier tube (PMT) was used to detect the PL.\textsuperscript{19-21} In TCSPC the arrival time of single photons are measured with respect to the laser excitation acting as a reference pulse. The reference pulse acts as a start signal and the photo-luminescence from the sample acts as the stop signal. The time difference between the start and stop signal is measured and stored. This process is repeated several times to have a complete decay curve of the photo-luminescence lifetime. The components required as shown in Figure 2.6 are excitation source (pulsed laser diode), monochromator, time-to-amplitude converter (TAC), constant fraction discriminator (CFD), multi channel analyser (MCA), PMT and computer based software for data analysis and fitting. The laser pulse from the excitation is source is divided into two parts; one part excites the sample whereas the other goes to a photodiode which generates the electrical signal for CFD. The CFD then generates the Start pulse for the TAC. Upon photo-excitation the sample emits photons which are collected at right angles with respect to the excitation source and are passed through a monochromator before
Figure 2.6. Schematically Depicting Different Components of TCSPC Instrument.

The signal from PMT is sent to CFD followed by TAC which acts as the Stop signal. The signal from TAC corresponding to the time difference between the Start and Stop signal is sent to the MCA which gives the numerical value of the time delay through an analogue to digital converter (ADC). The final output is counts vs. channel where each channel corresponds to a different delay. The photo-luminescence from the sample was detected at magic angle (54.7°) to avoid anisotropy effects. The maximum counts were kept 5000 to obtain good quality decay curves and the decay was recorded in the range 50-200 ns depending on the sample.

The decay traces were deconvoluted with respect to the instrument response function (IRF) and fitted with multiexponential functions \( I(t) = \sum a_i \exp \left(-\frac{t}{\tau_i}\right) \), \( \sum a_i = 1 \) where \( \tau_i \) is the decay time constant having amplitude \( a_i \) with least square fitting in the software keeping \( \chi^2 \) close to 1. The values of \( a_i \) and \( \tau_i \) were utilized to calculate the amplitude-weighted lifetime \(< \tau > = \frac{\sum a_i \tau_i}{\sum a_i} \) and time-weighted lifetime \( \tau_{av} = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \). The IRF of the instrument was found to be \( \sim 130 \text{ ps} \) from the light scattered by TiO₂ dispersed water. In QDs each of the exponential represents a radiative or non-radiative process.
2.3.2. Pump-Probe Transient Absorption Spectroscopy (TAS)

In the ultrafast TA spectroscopy\(^{22-26}\) the NCs were excited with 400 nm pump laser \((fwhm \sim 120\text{fs})\) and the pump induced changes in the absorption was probed with a broadband visible probe beam providing fundamental insight about the charge carrier relaxation and recombination dynamics. The basic experimental set-up of the TAS is shown in Figure 2.7 having Ti:sapphire oscillator, pulse stretcher, multipass amplifier, pulse compressor, pump-probe setup and the detection system each of which will be discussed in detail in the following sections.

![Figure 2.7. Outline of the Femtosecond Pump-Probe Transient Absorption Setup.](image)

2.3.2.1. Ti:sapphire Oscillator

The outline of the oscillator is shown in Figure 2.8. Ti\(^{3+}\) doped sapphire crystals are used as the gain medium whose absorption spectra ranges from 400-600 nm and the emission spectra ranges from shorter than 600 nm to more than 1000 nm. The Ti:sapphire crystal is placed at focus of spherical mirrors. The Ti:sapphire laser is an example of solid state tunable lasers (vibronic lasers). Due to the broad emission spectra adjustment of optical cavity length any output lasing wavelength can be tuned. The broad spectral range also helps to produce ultrafast pulses.
Figure 2.8. Layout of Ti:Sapphire Oscillator Used for the Transient Absorption Measurements.

Figure 2.9. Schematic of Four Level Ti:sapphire Laser. Upon photoexcitation (1) the electron moves from the ground state (GS) to the excited state (ES), where after non-radiative relaxation it comes to the lowest vibrational state (2). The lasing transition (3) takes place followed by non-radiative process (4) putting it back in the GS.

The states involved in the lasing transition as shown in Figure 2.9 are broad vibronic bands containing many vibrational sublevels which is the reason behind the spectral tunability. In our case the output was selected to be 800 nm. A diode pumped
continuous wave (CW) solid state laser (DPSS) with ~3.8W power excites the Ti:sapphire crystal at 532 nm.

For propagation of a Gaussian laser beam through a non-linear material at high intensity the refractive index changes non-linearly with the electric field:

\[ n(\omega) = n_0(\omega) + n_2(\omega)l(t) \]  

(2.32)

Here, \( n_2(\omega) \) is the nonlinear coefficient which gives the coupling strength between the refractive index \( n(\omega) \) and electric field \( l(t) \).

The intensity can be expressed as

\[ I(r) = \exp(-gr^2) \]  

(2.33)

Where, \( r \) is the beam radius and \( g \) is the shape factor. This implies the refractive index changes with the intensity of the laser beam and is maximum at the center than the sides. This self focuses the beam known as Kerr lens effect. The higher intense part of the beam are easily transmitted than the lower intense part. This power dependent loss makes the cw mode unstable. Short laser pulses are generated by introducing noise or disturbance in the system. This is known as Kerr lens mode locking as the mode locking results from the Kerr lens effect introduced in the nonlinear medium by the beam itself. The group velocity dispersion (GVD) as the beam repeatedly travels in the cavity, is compensated by placing two prisms. The polarization of the laser gets affected as the bi-refringent properties of Ti:sapphire crystal changes due to propagation of the intense laser beam. This can be avoided by placing the crystal at Brewster angle. The repetition rate \( (\tau_{rep}) \) is given by \( c/2L \) where \( c \) is the velocity of light and \( L \) is the cavity length. Ultrashort pulses (<10fs) is possible to generate due to broad PL band \( (\Delta t \sim \lambda^2/c\Delta\lambda) \) of Ti:sapphire crystal. The Ti-sapphire (TiS) oscillator used in our laboratory is TISSA 50 model (CDP, Avesta, Russia) which generates ~50fs pulses at 800 nm with 80-90 MHz repetition rate and 0.5 Joule (J) energy (~5nJ/pulse).

The output from the oscillator is used as a seed pulse for further amplification of power which will be discussed next.
2.3.2.2. Femtosecond Multipass Ti:Sapphire Amplifier

The amplification system (MPA 50, CDP, Russia) consists of pulse stretcher, pulse picker, multipass Ti:sapphire amplifier, pump laser, pulse compressor and electronics unit for required synchronization. This amplifier system typically provides \( \sim 10^5\) to \(10^6\) times amplification in power.

2.3.2.3. Pulse Stretcher

The seed pulse from TISSA-50 is first passed through a pulse stretcher for temporal stretching. The stretcher as shown in Figure 2.10 is an optical device that stretches femtosecond pulses to more than tens of picosecond pulses thereby reducing the peak power to avoid damage.

![Figure 2.10. Schematic Representation of Femtosecond Pulse Stretcher.](image)

of the active medium (Ti: sapphire in our case) in the amplifier. The diffraction grating within the stretcher sends longer wavelengths and shorter wavelengths of the seed pulse in different directions at different diffraction angles. The design is such that the shorter wavelengths have to travel longer enabling longer wavelengths to exit first temporally stretching the pulse. Four passes are made through the stretcher using the vertical retroreflector which sends the beam back to the stretcher to spatially reconstruct the beam.

2.3.2.4. Pulse Picker

The stretched pulses are sent to the pulse picker to decrease the repetition rate from 80-90 MHz to 1KHz. Here, a Pockel cell is placed between crossed polarizers. The
pulse from oscillator with horizontal polarization passes through the Pockel cell and exit the pulse picker in absence of voltage without amplification. When half-wave voltage is applied to the Pockel cell the polarization of the input pulse is changed from horizontal to vertical which passes through the polarizer and used as seed pulse for amplification.

2.3.2.5. Pump Laser and Synchronizing Electronics

Nd: YAG laser having 532 nm output is used as a pump laser (Jade, Thales Laser) in the amplification system with 1KHz repetition rate, 20mJ/pulse energy (maximum), <280 ns pulse width and horizontal polarization. Prior to amplification it is very necessary to select one pulse out of the pulse train for which synchronization electronics is utilized. The synchronization electronics triggers the required high voltage to the Pockel cell and also synchronizes with the pump laser having 1KHz repetition rate and the oscillator output. The pulse picker blocks the other pulses to enter the amplification system.

![Figure 2.11. Schematically Depicting the Mechanism of Pulse Amplification.](image)

2.3.2.6. Multipass Ti:sapphire Amplifier

After the pulse picker the seed pulse with 1KHz repetition rate enters the multipass Ti:sapphire amplifier system where a heavily Ti doped sapphire crystal is utilized as the gain medium. The seed pulse gains energy (amplification) while travelling through the gain medium where the pump laser (JADE) maintains population inversion, from the stimulated emission generated by itself (Figure 2.11). The outline of the amplifier is depicted in Figure 2.12 where due to the telescopic configuration of two concave mirrors having different radius of curvature allows eight passes of the seed pulse through the common focus where the gain medium (Ti:sapphire crystal) is placed. The
pump laser is also focused at the same spot on the Ti:sapphire crystal. During each pass the beam cross section decreases and the beam moves towards the center of the mirror from side and finally comes out of the amplifier.

Figure 2.12. Optical Layout of Two-Mirror Confocal Multipass Ti:Sapphire Amplifier.

2.3.2.7. Femtosecond Pulse Compressor

Figure 2.13. Layout Depicting the Basic Components of Femtosecond Pulse Compressor.

The amplified pulses are compressed to have the femtosecond pulses back. The compressor consists of two gratings and due to their arrangement the longer wavelength components have to travel more compared to the shorter wavelengths which is exactly opposite of the pulse stretcher, thus compressing the pulse to $\approx 100\text{fs}$ as outlined in Figure 2.13. After compressor the laser power is $\approx 0.2 \text{ mJ/pulse}$ compared to $\approx 0.5\text{ nJ/pulse}$ prior to amplification.
Second harmonic Generation: Generation of Pump Beam

The output pulse (800nm) is split through a beam splitter into a high intensity pump beam and low intensity probe beam. The pump beam (~100μJ/pulse) is then frequency doubled to 400 nm (~10μJ/pulse) which serves as the pump beam in all the TA experiments reported in this thesis with the help of a 0.5 mm thick β-barium borate (BBO) crystal. The frequency doubling or second harmonic generation (SHG) is a non-linear phenomena. The electric induction \( D \) within a material placed in an electric field \( E \) is expressed as

\[
D = E + 4\pi P
\]  
(2.34)

Here, \( P \) is the polarization of the medium. If the intensity of the light is small the polarization induced in the material is linear with respect to the electric field:

\[
P = \chi^{(1)} E
\]  
(2.35)

where, \( \chi^{(1)} \) is the first order electric susceptibility.

In intense electric field the relation does not remain linear and can be expressed as

\[
P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots
\]  
(2.36)

where \( \chi^{(n)} \) is \( n \)-th order susceptibility.

The second term in equation (2.36) is responsible for SHG effect. For a laser beam of frequency \( \omega_1 \) and wavevector \( k_1 \),

\[
E = E_0 \cos(k_1 r - \omega_1 t)
\]  
(2.37)

Therefore, the second order polarization can be expressed as

\[
P^2 = \chi^{(2)} E_0^2 \cos^2(k_1 r - \omega_1 t)
\]  
(2.38)

as \( \cos^2 x = \frac{1 + \cos 2x}{2} \) the equation (2.38) simplifies to

\[
P^2 = \frac{1}{2} \chi^{(2)} E_0^2 + \frac{1}{2} \chi^{(2)} E_0^2 \cos 2(k_1 r - \omega_1 t)
\]  
(2.39)

The second term in equation (2.18) which represents oscillations of polarization at \( 2\omega_1 \) generates the second harmonic at frequency \( 2\omega_1 \). To maximize the efficiency of SHG
the phase matching condition \((k_{SH}(2\omega)) = k_1(\omega_1) + k_1(\omega_1))\) or, \(n(2\omega_1) = n(\omega_1)\) needs to be satisfied. This implies the refractive index at \(2\omega_1\) must be equal to the refractive index at \(\omega_1\) for which birefringent crystals such as \(\beta\)-BBO is used.

### 2.3.2.9 Pump-Probe Spectrometer

In the pump-probe spectrometer, the layout of which is shown in Figure 2.14, the actual experiment of transient absorption occurs. The broad-band probe beam is generated by focusing the 800 nm laser pulse (~10 \(\mu\)J/pulse) on a sapphire crystal (1.5 mm thick). This is known as white light generation (WLG) which is the effect of self phase modulation (SPM). SPM is the most important mechanism through which new frequencies are generated from a fundamental frequency \((\omega_0)\) in a nonlinear medium. The electric field of the incident light beam propagating in \(z\)-direction is

\[
E_{in} = E_0e^{i(knz - \omega_0 t)} = E_0e^{i(\Phi_0)}
\]

(2.40)

As the non-linear index of refraction \(n(\omega)\) is dependent on laser pulse intensity following equation (2.11) as the pulse enters a non-linear medium of length \(L\), there is a intensity dependent shift in the phase \((\Phi)\) and the output electric field can be expressed as

\[
E_{out} = E_0e^{i(kn_0L + kn_2I(t)L - \omega_0 t)} = E_0e^{i(\Phi_{NL} + \Phi_0 t)}
\]

(2.41)

---

**Figure 2.14.** Schematic of Pump-Probe Transient Absorption Spectrometer.
The additional phase $\Phi_{NL}$ originates from the time dependent intensity $I(t)$. Due to the dependence of pulse frequency ($\omega$) on electric field as $\omega = -\frac{\partial (\Phi_{NL} + \phi_0)}{\partial t}$ the change in phase leads to modulation in the frequency generating a broad spectrum (Figure 2.15). In our case from fundamental 800 nm wavelength a broad probe beam of 440-1700 nm is generated using a sapphire crystal.

The pump induced changes in the absorption ($\Delta A = A_{pump\ on} - A_{pump\ off}$) was measured by splitting the probe beam to a sample (on which the pump overlaps) and reference beam both of which pass through the sample. The $\Delta A$ is calculated as:

$$\Delta A(\lambda) = -\log\left(\frac{I_{sample}}{I_{ref}^{pump\ on}}\right) + \log\left(\frac{I_{sample}}{I_{ref}^{pump\ off}}\right)$$

$$= -\log\left[\frac{I_{sample}}{I_{ref}^{pump\ on}}\right]$$

(2.42)

The pump power on the sample is controlled through a neutral density filter. The sample was put in a rotating cell of 0.1cm thickness and kept under constant rotation to avoid sample damage due to intense pump beam. All TA experiments were carried out at room temperature. The pump beam is passed through a chopper (500 Hz) so that every alternate pump pulse excites the sample. To avoid polarization effects the pump is sent through a polarizer kept at magic 54.7°. Prior to WLG the probe was sent through an
optical delay stage which controls the delay (0.66fs to 4ns) between the pump and probe. Upon pump-probe overlap within the sample and reference beam intensity was measured by CDP2022i imaging spectrometer and the calculated ΔA was plotted vs. wavelength and time using Excipro software. For fitting of the data Labview program was used. The temporal resolution of the data is measured to be ~100-120fs from the bleach signal of meso-tetrakis-(4-sulphanatophenyl) porphyrin dianion (TPPS aqueous solution at pH 1) at 710 nm following 400 nm pump excitation.

To compensate for group velocity dispersion chirp correction was performed on TA spectra. To correct for the chirp the arrival time of the probe (zero time) was measured from the instantaneous artifact signal of octadecene over the entire spectrum range. The zero time was plotted vs. wavelength and fitted with polynomial function which was used to generate chirp-free TA spectra. Chirp correction for each probe wavelength results same relative delay in the entire spectrum region.

2.3.3. Fluorescence Upconversion Measurements
The photo-luminescence decay in sub-picosecond timescale for CdSe and Cu-doped CdSe NCs (chapter 5) were monitored through femtosecond fluorescence upconversion instrument (FOG 100; CDP Inc., Russia) after exciting the sample at ~410 nm, 50fs, 88MHz and detecting the emission at the emission maxima. NCs dispersed in chloroform were rotated in a rotating cell of 0.4 mm width to avoid sample degradation due to pump.

2.4. Cyclic Voltammetric Measurements
The cyclic voltammetric (CV) measurements were performed in three electrode assembly with a working, quasi-reference, and counter electrodes. The potential at the working electrode is varied and the current flowing through it is measured. Starting from zero as the potential is made positive, the Fermi level moves down and loss of electron (oxidation) occurs leading to positive current peak if any matching state is present. On the other hand, if the potential is moved in the negative direction the Fermi level moves up leading to reduction current (Figure 2.16).
Figure 2.16. Representative cyclic Voltammograms for a QD showing the oxidation and reduction peaks corresponding to VB and CB, respectively.

The CV measurements help to determination the band-edge parameters and intra-gap states (trap states). The CV measurements were performed with the help of Biologic SP-300 Potentiostat/Galvanostat. A commercial Au-disk electrode (CHI Instruments, USA, 2-mm diameter), Silver wire, and Platinum wire loop were used as working, quasi-reference, and counter electrodes, respectively. Before the experiment, all the three electrodes were cleaned using dilute nitric acid. Especially Au disk working electrode was polished over 0.5 \( \mu \)m Alumina (Al\(_2\)O\(_3\)) powder and rinsed with copious amount of DI water. It was then further electrochemically cleaned by potentiodynamically cycling in 0.5 M H\(_2\)SO\(_4\) between the potential range 1.5V and -0.5 V (scan rate of 1000mV/s). As CV is very sensitive technique, before CV measurement it is very necessary to clean the working electrode. Because if the surface of the working electrode is contaminated it will show unwanted peaks and that will spoil the experiment. Even after polishing the Au disk electrode with 0.5\( \mu \)m Alumina powder the electrode is potentiodynamically cycled at high scan rate (i.e. 1V) until the characteristic peaks for Au is observed to clean the surface and ensured it is cleaned. To avoid the interference of atmospheric CO\(_2\) and moisture, the measurements were carried out in a homemade vacuum electrochemical cell, with a special provision to transfer the solvent. 0.341g of TBAP (typically, 100 mM stock 10 mL solution) was transferred first in the cell and vacuum-dried in-situ, at 80 °C.
for 2 hour. The cell was then cooled down to room temperature and brought to the atmospheric pressure by relieving the vacuum through high purity Nitrogen gas. Then 10 mL DCM (dried in CaH₂ overnight, double distilled and stored in molecular sieves) was injected into the cell through a silicone-septum under the Nitrogen atmosphere. For the controlled measurements, blank CV was recorded in the TBAP-DCM mixture without any sample. After that, the dispersion of NCs (1 mg/mL) 0.2 mL was introduced. At the end of each set of experiments, the potentials were calibrated with respect to the normal hydrogen electrode (NHE), using ferrocene as an internal standard. For NC cyclic voltammetry measurements scan rate of 100mV/s was used.

2.5. Quantum Dot Sensitized Solar Cell (QDSSC) Fabrication

For solar cell fabrication, QD sensitized TiO₂, polysulfide solution and copper selenide (Cu₂Se) were used as photoanode, electrolyte and counter electrode, respectively.

2.5.1. Phase Transfer of NCs

The NCs synthesized were capped by long-chain oleic acid surfactant. Therefore, in order to adhere it to the TiO₂ photoanode it was required to replace the long-chain ligand by a short-chain one. For this purpose NCs were phase transferred from non-polar to aqueous solvent using mercaptopropionic acid (MPA). The pH of MPA solution was adjusted to 12 by adding dropwise a solution of 40% KOH (basic) solution. At first, the NCs were precipitated by acetone to remove the excess surfactant. Then it was dissolved in minimum amount of chloroform. The MPA solution was added dropwise to it and vortexed continuously till the solution turned hazy. This symbolizes the ligand exchange. It was then centrifuged and the chloroform was decanted. After that the NCs were dissolved in minimum amount of water and precipitated again with acetone to remove excess MPA. Finally the NCs were dissolved in water and kept for further use.

2.5.2. Preparation of TiO₂ Photoanode

F:SnO₂ (FTO) coated glass (2cm x 2cm) with resistivity ~10Ω/square were cleaned by DI (de-ionized) water, soap solution and finally with ethanol in ultrasonic bath for 15 minutes each. In order to remove moisture it was dried at 150°C for 30 minutes.
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After that a transparent layer of TiO₂ (dyesol, DSL 18NR-T, average particle size 20 nm) was deposited on the conducting side of the FTO by doctor blade technique followed by sintering at 350°C for 10 minutes, at 450°C for 15 minutes and at 500°C for 15 minutes. Further a scattering layer of TiO₂ (dyesol, WER2-O, average particle size 150–200 nm) was deposited over the transparent layer and sintered again as the transparent layer. It was then allowed to cool down gradually to room temperature. The aqueous NC solution was dropcasted on the mesoporous TiO₂ film electrode and kept for an hour before rinsing it with DI water to remove the excess NCs. The NCs deposited TiO₂ film was then passivated by a quasi-shell of CdS through Successive Ionic Layer Adsorption and Reaction (SILAR) technique.

![Figure 2.17. Schematic Layout of QD sensitized TiO₂ Photoanode Preparation.](image)

For CdS layer, this was done by alternatively dipping the film into 0.1 M methanolic solution of Cd(NO₃)₂.4H₂O and 0.1 M methanol: water (1:1) solution of Na₂S for 1 min each and rinsing with DI water in-between each step. Six SILAR cycles were performed for each film. To overcoat with the CuS layer the photoanodes were dipped into a ~5.0 mM methanolic solution of CuCl₂. 2H₂O for variable amount of time ranging from 5s to 30s for cation exchange. For ZnS layer after CdS layer, the film was alternatively immersed in 0.1 M methanolic Zn(NO₃)₂. 6H₂O solution and 0.1 M methanol: water (1:1) solution of Na₂S for 1 min. Finally, the films were cleaned with DI water and dried in air. The whole procedure is presented schematically in Figure 2.17.
2.5.3. Synthesis of Cu₅Se (Counter electrode)

The Cu₅Se counter electrode was fabricated following procedures developed by Zhang et al.³⁰ Briefly, CuSO₄ solution (1 mmol in 10 mL of water) was added into Na₂SeSO₃ solution under stirring at room temperature for 5 minutes. The black precipitate was cleaned with DI water and ethanol for two times and kept in vacuum overnight for drying. The Na₂SeSO₃ aqueous solution was synthesized by heating 4 mmol of Se powder with 10 mmol of Na₂SO₃ in 40 mL DI water for 6 hours at 80°C. To make a uniform paste 0.2 gm of Cu₅Se was mixed with 1.0 gm terpinol and 2.0 gm of ethyl cellulose in anhydrous ethanol and sonicated for 20 mins. The solution was then deposited on the pre-cleaned FTO film and sintered at 450°C for 30 minutes followed by natural cooling.

2.5.4. Preparation of Electrolyte

A solution containing of 0.6 M Na₂S, 0.2 M S, and 0.2 M KCl was prepared by dissolving in 5 ml of 7:3 methanol-water mixture to obtain the polysulfide electrolyte.

2.5.5. Assembly of Solar Cell

The QD sensitized photoanode was sandwiched with the Cu₅Se counter electrode with polysulfide electrolyte (~150 μL) in between through binder clips.

2.5.6. Plasma Treatment on TiO₂ Photoanodes

For plasma treatment of the films the transparent TiO₂ coated films were exposed to the argon (Ar) plasma for variable amount of time ranging from 5-30 minutes. Then scattering layer of TiO₂ was coated on top of it and sintered at 450°C for 15 minutes and 500°C for 15 minutes. The details of the plasma set up are given elsewhere.³⁵ In short, this was a dielectric barrier discharge (DBD) of Argon gas which splits/transforms the moisture into hydrogen atom and H₂ to reduce the TiO₂. Argon Cold Plasma was generated in situ with (1.9 kV/mm) applied AC voltage at 50 Hz working frequency within double dielectric barrier discharge reactor (length 100 mm with volume capacity 11.5 mL) with two cylindrical and coaxial Pyrex surfaces: inner electrode outer diameter and thickness are: 7 mm and 1 mm respectively; the outer electrode inner diameter and thickness are: 14 mm and 1.5 mm respectively with discharge gas-gap 3.5 mm. Samples
were treated with the Ar plasma keeping at a distance ~1.5 ft /400 mm from the plasma zone.

To incorporate a hole transporting layer (HTL) of CuS along with passivating layer of ZnS, the 4 ML CdS coated films the following procedure was followed. The film was first dipped in 0.1 M Zn(NO₃)₂. 6H₂O solution in methanol for 1 minute, then in 1mM methanolic CuCl₂ solution for 5 s followed by dipping in 0.1 M (1:1) solution of Na₂S in 1:1 methanol water mixture for 1 minute. This was repeated for 2 cycles.

2.6. Characterization of the Solar Cell Devices

2.6.1. Current Density-Voltage (J-V) and Incident Photon to Current Conversion Efficiency (IPCE) Measurements

For the measurements of photovoltaic performance, current density versus voltage (J-V) curves were obtained for the solar cell assembly under 1 sun illumination (100 mW/cm²) using a G-short arc Xe lamp solar simulator (Peccell, model PEC-LOl) with a Keithley 2400 source meter. Using an action spectrum measurement system (Peccell, model: PEC-S20) with a xenon lamp (150 W) as the light source, incident photon-to-electron conversion efficiency (IPCE) measurements were carried out in the region of 300–800 nm.

2.6.2. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopic (EIS) measurements were performed on Biologic SP 300. For impedance measurements, the solar cell device was kept at a voltage close to Voc (0.5V) and a small 10 mV AC perturbation voltage \( V(\omega, t) = V_0 \sin(\omega t) \) with variable frequency \( f = \frac{\omega}{2\pi}, \omega \) is the angular frequency) ranging from 100 KHz to 0.1Hz under dark conditions were applied. The corresponding current \( i(\omega, t) \) at each frequency is measured.

The impedance \( Z \) is a complex quantity which can be calculated according to Ohm's law as
At a particular frequency the current can be expressed as:

\[ I(\omega, t) = I_0 \sin(\omega t - \theta) \]  \hspace{1cm} (2.44)

Here, \( I_0 \) is the current amplitude and \( \theta \) is the phase difference between current and voltage.

Using complex number notation the potential and current can be expressed as:

\[ V(\omega, t) = V_0 e^{i\omega t} \quad \text{and} \quad I(\omega, t) = I_0 e^{i(\omega t - \theta)}. \]

Therefore, the impedance can be expressed as:

\[
Z(\omega) = \frac{V(\omega, t)}{I(\omega, t)} = \frac{V_0 e^{i\omega t}}{I_0 e^{i(\omega t - \theta)}} = \frac{V_0}{I_0} e^{i\theta} = Z_0 e^{i\theta} = Z_0 (\cos \theta + i \sin \theta) \]

\[ = Z'(\omega) + i Z''(\omega) \]  \hspace{1cm} (2.45)

Here, \( Z'(\omega) \) (= \( Z_0 \cos \theta \)) is the real and \( Z''(\omega) \) (= \( Z_0 \sin \theta \)) is the imaginary part of the impedance \( Z(\omega) \).

---

**Figure 2.18.** Equivalent Circuit Representation of a Model QDSSC.

In Nyquist plot \( Z''(\omega) \) is plotted vs. \( Z'(\omega) \). In Bode plot phase \( (\theta) \) is plotted with respect to log of frequency. The EIS measurements have been widely used to model the QDSSCs to investigate the electron recombination and charge transport in different interfaces of the device. The equivalent circuit representation of the device is shown in Figure 2.18.
Considering the thickness of the TiO$_2$ layer to be $L$, electron transport resistance $R_{tr} (\approx r_{tr} L)$, the series resistance $R_s$ inferring the transport resistance of FTO and instrument, charge transfer resistance $R_{rec} = (r_{rec} - L)$ at the TiO$_2$/electrolyte interface which is inversely proportional to recombination rate, chemical capacitance $C_w (\approx c_w L)$ at the TiO$_2$/electrolyte interface inferring the change in electron density relative to the Fermi level, the charge transfer resistance $R_{CE}$ at the counter electrode/electrolyte interface and chemical capacitance $C_{CE}$ at the counter electrode/electrolyte interface can be obtained. $Z_d$ is the impedance related to the diffusion of redox ions through the electrolyte and is considered zero here. In Nyquist diagram (Figure 2.19) the semicircle in the high frequency (region I) and middle frequency region (region II) refers to the charge transfer processes in counter electrode/electrolyte (above 1kHz) and TiO$_2$/electrolyte interface (between 1kHz and 1Hz), respectively. At lower frequencies below 1Hz (region III), diffusion processes within the electrolyte contributes. Close to $V_{OC}$ the TiO$_2$ remains sufficiently conductive and $R_s$ becomes negligible and the simplified equivalent circuit has been considered for all EIS data analysis in the present thesis.

2.7. References


(40) González-Pedro, V.; Xu, X.; Mora-Seró, I.; Bisquert, J. ACS Nano 2010, 4, 5783.
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