Chapter 4

Experimental Techniques
EXPERIMENTAL TECHNIQUES

This chapter covers the detailed explanation of the experimental techniques employed to accomplish the objectives of this thesis. The present work is divided into eight parts as follows: extraction of MP fiber from the parent plant, interaction of fiber with X-ray radiation to confirm the stability of fiber, synthesis of CdSe-CdS core shell QDs and rod, coating of QDs on the surface of MP fiber, characterization of virgin and modified fiber, design and characterization of sensing plate (thin film) for detector application and fabrication of X-ray windowless detector. The major characterization techniques used to study the properties of virgin, high energy (6MV) irradiated fiber and quantum dots (CdSe-CdS core shell and rod) coated fiber are: X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) Transmission Electron Microscopy (TEM), I-V characteristics etc. In this chapter, each experimental technique has been described in lucid style under the following headings: instrumentation, sample preparation and experimentation.

4.1 Fiber Extraction Techniques

The *Mimosa pudica* plant was sourced from the local unmanicured gardens of Institute of Physics campus in Bhubaneswar. It is a small plant, about fifty cm long, and is abundantly found. Few stems of the plant were collected and about 10cm long pieces from them were sunk in 10% NaOH solution for one week, to extract the MP fiber. The as treated stem was removed from the dilute NaOH solution, and skins were carefully extracted. The treated fiber skins were gently pressed to clear residual solutions. These skins were thoroughly cleaned with running tap water and full lengths of the fiber were obtained. The samples were further sun dried and cut into the required size for irradiation and coating purposes. This fiber shall hence forth be referred as the ‘virgin fiber’.
Fig. 4.1 (a) Figure of *Mimosa Pudica* herb (b) Figure of *Mimosa Pudica* stem (c) Figure of *Mimosa Pudica* single plant stem (d) Figure of *Mimosa Pudica* stem dipped in NaOH solution

Fig.4.2 (a) Figure of *Mimosa Pudica* stem dipped in NaOH solution after 7 days (b) Figure of *Mimosa Pudica* fiber just cleaned with running tap water
4.2 Characterization of virgin MP microfiber

X-ray Diffraction, Scanning Electron Microscopy and I-V characteristics study was conducted for characterization of virgin MP fiber samples:

4.2.1 X-Ray Diffraction (XRD)

The X-ray analysis of polymer is often more difficult than other classes of solids because of the following reasons [39,83-112] viz. it is difficult to grow large crystals, intensity obtained is less and it falls off rapidly with diffraction angle (2θ) because of weak bonding, leading to large temperature variation coefficient, etc. The most important parameters in X-ray diffraction studies are inter-planer distance (d), intensity of the diffraction peaks and FWHM. The above parameters can be accurately estimated by using sophisticated instrument and profile fitting program.

Instrumentation

The experimental setup used for this study consists of a grazing incidence X-ray diffraction (GIXRD) instrument, (Bruker AXS, D8 ADVANCE™ X-ray instrument) operated with monochromators in non dispersive arrangements in parallel beam geometry. Incident line focussed CuKα radiation from a high-power X-ray tube was operated at 1600 W (40kV and 40mA) using a KRYSITLLO 780 X-ray generator. Again, the source with the Be-window of the high power tube having 95% transmissions emits CuKα. The CuKα radiation from the line focus tube was collimated through fixed divergence slit of 6mm (=10°) before irradiating the sample. The scattered X-ray beam from the sample was well collimated by
passing through slits. It then gets reflected by LiF (100) crystal monochromator \((d = 2.2265 \text{ Å})\). A NaI dynamic scintillation counter of quantum yield around 95% was mounted on the goniometer. The step size chosen was 0.05° with scan rate of 0.05°/min (step). Analysis of results was done by the accompanied software supplied by Bruker AXS, USA.

**Sample Preparation:**

The virgin MP natural fiber sample, prepared as per the procedure described earlier was mounted on the sample holder. One thus gets a flat sample of uniform length, breadth and thickness, because of the dimension of the sample holder, for each test sample, for X-ray diffraction analysis.

![Bruker AXS, D8 ADVANCE™](image)

**Experimentation**

The X-ray diffraction patterns for the virgin fiber were recorded with a step size of 0.01° on a 3°-55° range with a scanning rate of 0.0083°/sec. The diffractometer injects line focused and collimated \(\alpha\) - radiation from the X-ray tube operated at 40 kV and 30 mA through fixed divergence slit of 0.5° and 10 mm mask. The radiation then gets diffracted from the fiber sample. Then the diffracted beam from the sample was collimated as it passes
through a programmable anti-scattering, receiving and soller slits. The diffracted beam is then reflected by the graphite monochromator. Experimental data such as d spacing, area or the diffraction peak and intensity were calculated using X’pert Graphics & Identify software [92]. Also, the refined and fitted X-ray profile was calculated using Profit software.

4.2.2 Scanning Electron Microscopy (SEM)

The SEM analysis on the fiber sample was conducted to produce the images of the fiber sample containing information about the fiber sample composition and surface topography [99-102].

Instrumentation

A JEOL-JES 6480 LV, Japan-made SEM, resolution 3 nm, magnification: < 5-100000 X was used to investigate the topography of virgin MP fiber. The near to the ground vacuum form allows for surveillance of sample which cannot be viewed at far above the ground vacuum due to extreme water content or due to a non-conductive surface. Its asynchronous five axes automatically eucentric phase by means of component sequential turning round and tip can house a sample of up to 8 inches in diameter. Criterion automatic kind comprise Auto Focus/Auto Stigmator, Auto Gun (diffusion, prejudice and position), plus routine difference and intensity.

Fig.4.5: JEOL-JES 6480 LV, Japan-made SEM
The parameters of JEOL-JES 6480 LV are Resolution High: Vacuum mode: 3.0 nm (30kV), Accelerating Voltage: 0.3 to 30 kV, Magnification: x5 to 300000, Objective Lens: Super Conical lens, Maximum Specimen Size: 8” coverage, 12” specimen can be loaded. Filament: Pre-cantered W hairpin filament and goniometer: X=125mm, Y=100mm, Z=5 to 80 mm, T=-10 to 90°, R=360° (endless).

Sample Preparation

All the MP fiber samples have been coated with 80 nm graphite layer by vacuum evaporation method [101].

Fig.4.6: Schematic diagram of JEOL-JES 6480 LV, Japan-made SEM
Experimentation

An electron beam or 5 kV and 41 μA has been used for SEM analysis of the virgin MP fiber samples. The graphite coated fiber was mounted in two different modes (lateral and cross sectional modes) as defined below for the investigation. An electron beam or 5 kV and 0.5 mA was used for the study of graphite coated fiber mounted in cross sectional mode.

4.2.3 I-V Characteristics

The transport of the charges in a natural conducting polymer under the influence of an electric field, and also as a result of a non-uniform concentration gradient is investigated. If a constant electric field $E$ (volt/m) is applied to the polymer, as a result of this electrostatic force, the electrons would be accelerated and the velocity would increase indefinitely with time.

Instrumentation

A special type of instrument fabricated for conductivity measurement of the microfiber which was followed by typical type of a sample holder of microfiber, a voltmeter, and ammeter with low biasing voltage followed by a rheostat.

Sample Preparation

All the MP fiber samples are of equal dimension prepared for conductivity measurement of length 10 cm placed carefully on the surface of the sample holder.

Sample

The MP natural fiber sample was mounted on a special type of fiber sample holder to form a flat sample of uniform length, breadth and thickness in each test sample for X-ray diffraction study. Again, for the electrical conductivity study, single filament of 1cm length was taken from the samples and mounted in the sample holder for measurement of resistance and resistivity of natural fiber.
Fig.4.7: Schematic diagram of special type of instrument fabricated for conductivity measurement equipment.

**Experimentation**

The electrical characteristics have been studied for the single fiber at low bias voltage (0-36V). The I-V characteristics plots of single fibers were carried out with variable potential.

**4.3 Irradiation of fiber through linear accelerator (LINAC)**

A linear accelerator (LINAC) is a machine which produces high energy X-rays (MV) and electron beams (MeV) equipped with multi leaf collimator (MLC) used as blocking device and most commonly used for high precision external beam line. The establishment of radiation is based on the interaction between matter and radiation energy. Thus interaction between radiation and matter translates the science of radiation physics [102]. The production of radiation using sophisticated devices like LINAC is very interesting and provides useful informations concerning interaction with matter. The radiations produced by LINAC have many advantages over the traditional X-ray machine or Cobalt-60 unit. The LINAC uses microwave technology (similar to that used for radar) to accelerate electrons in a part of the accelerator called the wave guide (WG). The WG structure is energized at microwave frequency most commonly at 3000 MHz (100 mm wave-length in free space) [103], then allows these accelerated electrons to collide with a heavy metal target as a result of which high-energy transmission X-rays are produced.
from the target. These X-rays are directed towards the matter and the beam comes out of the accelerator through gantry, which rotates around the position of matter. Outcome of radiation beam is directly related to the precession in the delivered dose to the sample that is dependent on the accuracy of beam data used in the treatment planning process. These data are obtained from the LINAC and are treated as the standard data and should be verified periodically as described by Task Group-40 protocol [104]. This LINAC has dual energy photon beam (6MV and 15 MV) and multi energy electron beam (4, 6, 9 and 12 MeV) with MLC facility. In this work we used some dissymmetric equipments, like 3D water phantom scanner with computer interface called as radiation field analyzer (RFA-300), ionization chambers (two cylindrical and one flat), and Dose-1 electrometer (all instruments are from Scanditronix-Wellhofer Company, Germany), solid phantom radio chromic films (EDR2), film laser scanner, barometer, chronometer and thermometer. The 3D water phantom called as radiation field analyzer (RFA-300) and controlled by Omni Pro-accept computer software was used for depth-dose, beam profile, penumbra, and is dose measurements. The RFA-300 consists of a cubic water tank with inner dimensions of $58 \times 58 \times 58$ cm$^3$. Film scanners are used to convert the film data to digital data by using computer software, which gives finally the intensity of the incident beam at various points in the radiation field. The positional accuracy of the drive mechanics of the water phantom was ± 0.5 mm, and the reproducibility was 0.1 mm (supplied value, RFA-300 Plus System Manual, 1998). Air cavity ionization chamber is the detector of choice for the radiation measurement, as its measurement response is independent of the fluence of the beam characteristics (beam quality, dose and dose rate) and shall possess good reproducibility and repeatability. The radio chromic film gives practical and rapid indications of the dose distribution in a plane. The advantage of the film lies in its high spatial resolution, which is particularly useful in regions where dose gradient is very high.

**The Photon Source**

The correspondence between optical and radiation fields of photon beam was assessed, at the depth of reference plane (at dose maximum depth). The reference plane was placed at its centre of the accelerator for square fields $5 \times 5$ cm$^2$, $10 \times 10$ cm$^2$ and $30 \times 30$ cm$^2$ with gantry position of $0^\circ$ for each photon nominal energy (MV). In all cases, the separation between optical field edge and the 50% iso-dose was found to be ≤
2 mm for all field dimensions. For the radiation field flatness, transverse beam profiles were obtained at the depths of maximum dose position ($d_{max}$) and 10 cm along the two orthogonal axes and diagonal axis of the beam. From the respective beam profiles, maximum ($V_{max}$) and minimum ($V_{min}$) values of dose in the central 80% region were obtained [105]. The required field flatness parameter ($V$)

$$V = \left(\frac{V_{max} - V_{min}}{V_{max} + V_{min}}\right) \times 100$$

(11)

The values of $V$ calculated, were found to lie within ± 3%. Radiation field symmetry, shows the uniform intensity of beam at all points across the radiation field; it means the ratio between measured values for each pair of symmetrical points (with respect to beam axis) for a range of field sizes must lie between 0.97 and 1.03 within the central 80% flattened beam area [106-107]. The actual output dose is also known as absolute dosimetry, in which, it is required to measure the output of different FSs ($5 \times 5, 10 \times 10, 15 \times 15, 20 \times 20, 25 \times 25$ and $30 \times 30$ cm$^2$) by placing an ion chamber on the central axis of the beam in a water phantom (40×40×40 cm$^3$) at measuring distance [(MD = SSD + water depth =100 cm +10 cm)] for all photon energy. The approximate flux of the source are of the order $10^{18}$ photons/sec and $10^{20}$ electrons/sec with a highest delivery dose rate of 500 Gy/min for photons and 400 Gy/min for electrons at the dose maximum point in the water phantom.

**Experimentation**

The extracted fiber sample material was irradiated using a medical linear accelerator LINAC (Elekta, UK) at Hemalata Hospitals & Research Centre (HHRC), Bhubaneswar. Using 6 MV, X-ray photon extracted from the above LINAC, the fiber was irradiated at a rate of 400 MU/min for get a dose of 10Gy, 15Gy, 20 Gy and 25Gy.
Sample preparation

The MP natural fiber sample and irradiated samples were mounted on a special type of fiber sample holder to form a flat sample of uniform length, breadth and thickness in each test sample for X-ray diffraction study. Again, for the electrical conductivity study, single filament of 1cm length was taken from the samples and mounted in the sample holder for measurement of resistance and resistivity of natural fiber.
4.4 Characterization of irradiated microfiber

4.4.1 X-Ray Diffraction (XRD)

The experimental setup consists of grazing incidence X-ray diffraction (GIXRD) instrument, (Bruker AXS, D8 ADVANCE™ X-ray instrument) operated with monochromator in non-dispersive arrangement in parallel-beam geometry. Incident line focus CuKα radiation from a high-power X-ray tube was operated at 1600 W (40 kV and 40 mA) using a KRYSTALLO 780 X-ray generator. Again, the source with the Be-window of the high power tube having 95% transmissions emits CuKα. The CuKα radiation from the line focus tube was collimated through fixed divergence slit of 6 mm ( =1°) before irradiating the sample. The scattered X-ray beam from the sample was well collimated by passing through Soller slit of 0.23° before getting it reflected by LiF (100) crystal monochromator (d =2.2265 Å). A NaI dynamic scintillation counter of quantum yield around 95% was mounted on the arm of the goniometer circle of radius 300 mm. Step size chosen for this experiment was 0.05° with scan rate of 0.05°/min (step) and analyzed using the software supplied by Bruker AXS, USA.

4.4.2 Scanning Electron Microscopy (SEM)

The electron microscopic techniques used for the characterization of above defined fibres have been discussed.

4.4.3 I-V Characteristics

The electrical characteristics have been studied the characterization of above defined fibers have been discussed.

4.5 Synthesis of CdSe-CdS nano Phosphors

The multi constituent nanostructures and their synthesis of have developed rapidly over recent years. The group II-VI semiconductor nano-heterostructures has been synthesized with a variety, counting spherical core-shell particles, seeded nanorods, and seeded tetrapods. These heterostructures permit for complicated manipulation of photons and carriers at the nano scale and show many attractive phenomena with very high death coefficients, polarized emission and high quantum yields. It requires exact organize over the composition, phase, shape, dimension, and connectivity of each component of synthesis nano crystals.
Organize above these a variety of factors relies mainly on the aptitude to separately adapt the speed of nucleation and growth [108-115]. Single scheme to attain self reliant organization over nucleation and growth is to divide these two processes into separate synthetic steps. The minute differences in the methods and reagents in employment in nanoparticle syntheses have been shown to make spectacular differences in the finishing product. Basically we have reported synthesis of three types of nano phosphors for our experimental requirement. These are:

A) CdSe-CdS core shell QDs

B) CdSe/CdS dot-in-rod

C) Seeded CdSe/CdS QDs rod

**Experimentations**

**4.5.1 Synthesis of CdSe-CdS core shell QDs**

First, Wurtzite CdSe core QDs of 3.5 nm in size were synthesized applying hot-injection technique as described in Carbone *et al.* [111,131]. These QDs were used as seeds for the growth of a CdS shell recently reported in Gomes *et al.* [130]. The nanocrystals were purified by the addition of isopropanol and methanol, centrifugation at 3000 rpm for 10 minutes and redispersion in toluene. The purification was continued for three times.
Fig. 4.9 Schematic diagram of 3-neck round bottom flask equipped with Degas
the mixture at 150 °C under vacuum for 1 hr while stirring (800 rpm).

4.5.2 Synthesis of CdSe/CdS dot-in-rod

The synthesis of CdSe-CdS quantum dot-in-rods was carried out using the hot-
injection technique as synthesised in Carbone et al. [111]. The CdSe-CdS quantum dot-in-
rods are made of a CdSe spherical core (dot) embedded in a rod such CdS shell (rods). The
above nanocrystals were purified by the addition of iso-propanol and methanol, applying
centrifugation technique set at 3000 rpm for 10 minutes with redispersion in toluene. The
purification was repeated three times. The sizes of the dot-in-rods structures were determined
by high-resolution microscopic analysis.

4.5.3 Synthesis of Seeded CdSe-CdS QDs rod

The synthesis of high luminescence of Seeded CdSe/CdS QDs rod was carried out by
hot-injection technique as synthesised in Carbone et al. [111]. The upper part of nanocrystals
was purified by adding iso propanol and methanol, applying centrifugation method set at
3000 rpm for 10 minutes time. Then it was dispersed again in toluene. The sizes of the Seeded CdSe/CdS QDs rod structures were determined by high-resolution microspectroscopic analysis [117-125].

4.6 Characterization of nano-phosphors

4.6.1 Transmission Electron Microscopy (TEM)

In the advancement of materials science and engineering, it is necessary to observe, analyze and understand the phenomena occurring at the nano regime. The transmission electron microscope (TEM) is a powerful and versatile instrument which permits characterization of materials [126] to obtain information from different modes, like, bright field and dark field imaging, used to characterize defects and domain structures. Information from selected area diffraction (SAD) and high resolution TEM analysis, from reconstruction of the reciprocal space gives information about the crystal structure and identifies different phases. The first TEM was reported to be built by two German scientists, M. Knoll and E. Ruska, in 1932 [128].

In a TEM, a high-energy (~200-300 keV) electron beam and its interaction with the specimen generates the image of the specimen at an atomic scale. To get an insight of crystallographic information available using TEM, both imaging and diffraction modes are used regularly. For direct information of defect structure on the atomic scale, an HRTEM is particularly useful with low spherical aberration coefficient (or with aberration correction), given that this is the typical spacing between atoms in solids [127].

Instrumentation

A transmission electron microscope, similar to a conventional microscope has a three stage system: illumination system, specimen stage and imaging system. An electrostatic lens in the form of Wehnelt cap is used after the filament to converge the maximum number of emitted electrons. An electron source, acceleration column and a condenser lens constitutes the illumination system. The illumination system projects an electron beam on the mounted specimen, or experimental object. In this thesis, most of the TEM measurements have been carried out using JEOL 2010 TEM operating at 200 keV with LaB₆ thermionic emission gun. Here, high voltage is generated in a separated power supply unit using Cockcroft-Walton technique and is coupled with the accelerating column. Following the acceleration column,
condenser lens system is situated. Electrons are generated in the electron gun by thermionic emission, where the filament material is heated to a suitable temperature. The filament emits electrons once the temperature induced energy overcomes the work function (\(\varnothing\)) of the filament material (according to \( J = AT^2 e^{\frac{\varnothing}{k_B T}} \), where \( J \) is the current density at the tip, \( A \) is Richardson's constant and \( k_B \) is Boltzmann constant). Being fired from the electron gun, electrons are accelerated towards the anode to enter the column. With a velocity closer to the speed of light, and with energy of 200-300 keV, the wavelengths of the electrons need to respond for relativistic effects through:

\[
\lambda = \frac{h}{\sqrt{2m_0 eV \left( 1 + \frac{eV}{2m_0 c^2} \right)}}
\]

It is to be noted that, corresponding relativistically corrected wavelength \( \lambda \) for 200 keV electrons is 0.0025 nm. Electrons are made to accelerate towards the anode at the top of the column and focus at the specimen with the help of condenser lens system, where the later sends a parallel or convergent beam of electrons towards the specimen. In practice, a complete parallel beam is not possible and the beam always possesses a certain kind of convergence when imaging at high resolution, usually in the range of \( \approx 1 \) mrad for LaB\(_6\) emitters. Using different sizes of condenser aperture, illuminated area of the specimen can be changed. Objective lens (OL) is located below the specimen. The combination of intermediate and projector lenses are used to obtain the desired image magnification. After the objective lens, objective aperture and selected area diffraction aperture are placed as shown in Figure 4.10. To record the magnified image or diffraction pattern formed at the phosphor screen, photographic films or charge coupled devices or their combinations are used. The recorded image on the phosphor screen is channeled to the CCD, whose output is connected to the computer using the image processing system. As electron is a very highly interacting particle, therefore vacuum pressure maintained inside the column of TEM, is \( \approx 10^{-8} \) mbar.

When the electron beam enters the specimen, most of the electrons get elastically scattered by the nucleus of the specimen atoms. The remaining electrons pass through an inelastic scattering by the electrons in the specimen. In comparison to X-ray diffraction or neutron diffraction, since interaction of electrons with the specimen is of considerably high,
multiple scattering processes dominate. To avoid dominance of such multiple scattering, a very thin specimen is used.

Small, localised reductions in wavelength occurs, resulting in phase change of the electrons, as the electron beam passing through the specimen interact with the nuclei of the specimen. Desired information about the specimen structure is therefore transferred to the phase of the electrons. The elastically scattered electrons are responsible for formation of the high resolution images, whereas, inelastically scattered electrons contribute mostly to the image. However, information about the chemical composition of the specimen can be obtained from the electron energy loss spectrum of the inelastically scattered electrons. The inelastically scattered electrons also produce Kikuchi lines in the electron diffraction pattern that is helpful for accurate crystallographic alignment of the crystals in the specimen.

**Interaction of electron with the specimen**

![Schematic diagram of different processes taking place during electron solid interaction.](image)

Fig. 4.10: A schematic diagram of different processes taking place during electron solid interaction.
Imaging and Diffraction

The conventional TEM image formation for thicker specimen is very similar to the projector principle, in this case, an incoherent particle model can describe the interaction of the electrons with the specimen. Specimen contains variation in thicknesses and density. So, the electrons will lose more energy when they transmit through the thicker and denser region and hence it will appear as darker object. Same way, the thinner region will appear as brighter object. This contrast in imaging mode arises due to variation of thickness and is referred as mass-thickness contrast. In *diffraction contrast*, contrast depends upon the crystallinity of the specimen. However, for thin specimen at high resolution, this description fails because the wave nature of the electrons is then needed to be invoked. If the specimen is thin enough and crystalline, then elastic scattering is usually coherent and these scattered/transmitted electrons are contribute to the image formation. After the exit of electrons (elastically transmitted coherent electron beams), the diffraction spots and image are used to form at back-focal plane and image plane of objective lens (OL), respectively. The diffraction pattern can be understood by taking the fast fourier transform (FFT) of the wave function of electron at the back focal plane of OL. The lattice image will form due to interference between the direct and diffracted beams depending on the phase difference between these two. So the highly diffracted beams are used to cut down by the objective aperture. The resolution and the details of image formation are governed by the contrast transfer function (CTF).

To retrieve structural information of the specimen from the micrograph, it is necessary to calculate the trajectory of the electron wave through the specimen. In the kinematical approximation, multiple scattering of the electrons in the sample is ignored resulting in an undisturbed central beam. This approach already fails at a small thickness or a single atom. In dynamical calculations all the scattered beams and their mutual exchange of intensity during the course of multiple scattering in the specimen are taken into account. It is possible to do full dynamical calculations but these are soon limited by the available computing power. Using the fact that the vast majority of the electrons are scattered in a forward direction with small diffraction angles Cowley and Moodie devised the multi slice approximation [129].

In this work, two kinds of TEM systems have been used. Majority of TEM has been carried out using JEOL 2010 TEM operating at 200 keV at Ghent University, Ottergemsesteenweg 460, 9000 Ghent, Belgium. This machine is equipped with an ultra high resolution pole piece (UHR-URP22) (spherical aberration coefficient (C_a) of 0.5 mm) and can have a point-to-
point resolution of 0.19 nm. For recording images and diffraction patterns charge coupleddevice (CCD) based detector with 4008 x 2672 pixels (Model 832, Gatan Inc.) has been used. In this thesis work, STEM, EDS and 3D tomography were carried out with a 300 keV electrons in the C$_2$-corrected FEI Titan 80/300 system at the University of Bremen, Germany. A probe diameter of 0.2 nm was used during HAADF and STEM-BF measurements.

**Sample preparation**

Sample preparation is one of the important aspects, where a lot of care needs to be taken for carrying out good TEM measurements. As the electrons transmit through the specimen, the specimen has to be thin enough to allow the electrons to pass through the sample. For conventional TEM, thickness needs to ≈100 nm and even lesser thickness (<10 nm) for HRTEM imaging. Two types of samples are prepared depending on the interest of study: Cross-sectional TEM (XTEM) sample (required to probe the interface and/or bulk solid), and planar TEM specimen preparation (probe the surface morphology).

**Planar specimen**

For Planar TEM sample preparation, a 3 mm disc was cut from the desired substrate using ultrasonic disc cutter and thin down to ~ 100μ using the lapping and polishing system. Here, the mechanical thinning starts with a larger grit size and finished with finer grit size. Then the specimen is dimpled to lower the thickness at the center (down to 30-40 μm) and polished using dimple grinder (DG) system (model 656, Gatan, USA). In this process, the edge remains thicker but center part becomes thinner. Electron transparency of this dimpled sample is achieved by ion milling using precision ion polishing system (PIPS) (model 691, Gatan, USA). During ion milling process, a 3.0 keV Ar ion beam is used to sputter the material from the specimen in grazing incidence (4°-7°). A Gentle million milling system (Technoorg Linda) is also used for further thinning with much lower energies (200-400-eV Ar ions).

**Cross sectional specimen**

For cross sectional TEM sample preparation, two rectangular pieces of size (2.5 x 3) mm$^2$ each were cut from the desired sample using abrasive slurry wire saw (model 850, SBT). These pieces were pasted face to face using epoxy (Gl epoxy, Gatan, USA) as close as possible. It will ensure an optimal ion milling rate i.e. if the glue quantity will be too high, the
ion mill will remove it quicker than the sample resulting a sharp hole with a sharp edge, opaque to electron beam, so care is taken to have enough material. Following this, the sample is inserted into a stainless steel tube having inner and outer diameter 2.5 mm and 3 mm respectively. After setting in, a 1 mm slice is made using low speed diamond wheel saw (model 650, SBT). The slice is thinned mechanically (by lapping and dimpling) followed by 3.0 keV Ar ion milling to achieve the electron transparency. The procedure for thinning XTEM sample is also like planar specimen but in this case one needs to do the lapping from both sides and dimpling for one side. The procedure of cross-sectional specimen is pictorially explained in Figure 4.13 and 4.14, along with the instruments used for the same. Mechanical thinning of the sample from both sides followed by dimpling on one side will be taken to the PIPS to obtain the electron transparency.

Fig.4.11: Schematic diagram JOEL JEM-2010 Transfer electron Microscopy at Physics and Chemistry of Nanostructures, Ghent University, Ottergemsesteenweg 460, 9000 Ghent, Belgium
Fig: 4.12: A schematic diagram of procedure to prepare a typical planner TEM specimen.

Fig: 4.13: A schematic diagram of procedure to prepare a typical cross-sectional TEM specimen.
4.6.2 Photoluminescence (PL) Spectroscopy

Another useful technique called as Photoluminescence Excitation (PLE) Spectra have been adopted to explore the optical properties of semiconductor QDs. By using this technique, for scanning the excitation energy a narrow spectral region of the luminescence is monitored. The luminescence from smaller QDs is monitored by probing the high-energy emission end of the luminescence. So it helps to removing the size distribution broadening effect on the absorption of QDs and assists in assigning the discrete optical transitions.

Instrumentation:

Absorption spectra CdSe-CdS core shell quantum dots (QDs) of were taken using a Perking Elmer Lambda 950 spectrometer. Photoluminescence (PL) measurements of sample were done on an Edinburgh Instruments FLSP920 UV-vis-NIR spectro-fluorimeter, using a 450W xenon lamp as the steady state excitation source and a Hamamatsu R928P PMT detector, which has a response curve between 200 and 900 nm. All emission spectra were recorded for an excitation wavelength of 365 nm and were corrected over the sensitivity of the detector. Photoluminescence quantum yields of the samples were measured for an excitation wavelength of 365 nm and using an integrating sphere.

Sample Preparation

The aggregation state of the sample, with the scattering contribution increasing as the particles aggregate to a greater extent is typically very sensitive to Scattering from a sample. When particles aggregate and the conduction electrons near each particle, surface become delocalized and are shared amongst neighbouring particles the optical properties of nanoparticles changes. And the surface plasmon resonance shifts to lower energies, causing the absorption and scattering peaks to red-shift to longer wavelengths. A simple and reliable method for monitoring the stability of nanoparticles solutions can be used as in UV visible spectroscopy.
Experimentation

Absorption spectra CdSe-CdS core shell quantum dots (QDs) of were taken using a Perking Elmer Lambda 950 spectrometer. Photoluminescence (PL) measurements of sample were done on an Edinburgh Instruments FLSP920 UV-vis-NIR spectro-fluorimeter, using a 450W xenon lamp as the steady state excitation source and a Hamamatsu R928P PMT detector, which has a response curve between 200 and 900 nm. All emission spectra were recorded for an excitation wavelength of 365 nm and were corrected over the sensitivity of the detector. Photoluminescence quantum yields of the samples were measured for an excitation wavelength of 365 nm and using an integrating sphere. For the electrical conductivity study, single filament of 1cm length was taken from the samples.

4.7 Coating of nano-material on the surface of MP fiber and fabrication of sensing plates (Thin film)

The MP fiber was arranged in regular parallel lines on a polymer substrate. The CdSe-CdS quantum dots-in-rods and CdSe-CdS core shell QDs particles were then deposited on the
surface of the MP fiber by the chemical dipping method. Perfect control is possible over the nano-particles in terms of size, shape, and smooth surface of CdSe-CdS core shell QDs particles coated with MP fiber by chemical dipping method. The analysis of nano-particles in terms of size, shape, and surface smoothening established the importance and particle surface area for the prediction of nanoparticles consistency. The method of fabrication included the following steps. First, the MP fiber was made arranged in a regular line with a polymer substrate with centres opening (10×10 cm²); all fibers were arranged in a line. CdSe-CdS QDs particles were then deposited on the surface of the MP fiber by chemical dipping method. A copper electrode was then deposited on the front (quantum dot side) and the back of the wafer. Finally, wires were connected to the top and bottom fiber electrode using conductive silver paint.

4.8 Characterization of sensing plate (Thin-film) for sensing application

4.8.1 X-Ray Diffraction (XRD)

The experimental setup consists of grazing incidence X-ray diffraction (GIXRD) instrument, (Bruker AXS, D8 ADVANCE™ X-ray instrument) operated with monochromator in non-dispersive arrangement in parallel-beam geometry. Incident line focus CuKα radiation from a high power X-ray tube was operated at 1600 W (40 kV and 40 mA) using a KRYS TALLO 780 X-ray generator. Again, the source with the Be-window of the high power tube having 95% transmissions emits CuKα. The CuKα radiation from the line focus tube was collimated through fixed divergence slit of 6 mm (=1°) before irradiating the sample. The scattered X-ray beam from the sample was well collimated by passing through Soller slit of 0.23° before getting it reflected by LiF (100) crystal monochromator (d =2.2265 Å). A NaI dynamic scintillation counter of quantum yield around 95% was mounted on the arm of the goniometer circle of radius 300 mm. Step size chosen for this experiment was 0.05° with scan rate of 0.05°/min (step) and analyzed using the software supplied by Bruker AXS, USA.

4.8.2 Scanning Electron Microscopy (SEM)

The electron microscopic techniques used for the characterization of above defined fibres have been discussed.
4.8.3 I-V Characteristics

The electrical characteristics have been studied the characterization of above defined fibers have been discussed.

4.9 Sensing plates (Thin-film) as a window-less X-ray detector

Photo-sensing plate

For photodetecting measurements, a special type sensing plate (thin film) fabricated using virgin and CdSe-CdS core shell QDs, CdSe-CdS quantum dot-in rod and Seeded CdSe-CdS QDs rods coated on the surface of MP fibers. These sensing plate (thin film) samples are:

- Sensing plate without coating
- Sensing plate coated with CdSe-CdS core shell QDs
- Sensing plate coated with CdSe-CdS QDs dot-in-rod
- Sensing plate coated with Seeded CdSe-CdS QDs rod

4.10 Photo-sensing plate with incidence of X-rays

An experiment was conducted to access the X-ray based photo amplification characteristics by allowing 17 keV-rays X-ray (MoKα) to irradiate the CdSe-CdS core shell, quantum dot-in-rod, Seeded QDs rod coated MP fiber samples for sensing application. The schematic diagram of the photo sensing plate with incidence of X-ray is shown in Figure 5.28. The electric current was detected by applying variable potential source through pico-Ammeter. The forward and reverse biasing current was read through a rheostat and shunt arrangement in the circuit with and without incidence of X-ray.

4.10.1 I-V Characteristics

Another useful technique called as Photoconductivity Measurement has been adopted to explore the optical properties of semiconductor QDs. By using this technique an experiment was conducted to access the X-ray based photo amplification characteristic possess, 17 KeV-ray (MoKα) allow irradiating the sample.

The various experimental techniques used for the characterization of virgin, irradiated and coating M.pudica fibre samples are as follows:
Sample Preparation

For the electrical conductivity study, single filament of 1cm length was taken from the samples and mounted in the sample holder for measurement of resistance and resistivity of natural fiber and CdSe-CdS core shell quantum dot (QDs) coated fiber. And for photo detecting measurement, we prepared a fabricated a special type sensing plate using virgin and CdSe-CdS Core shell QDs particle coating MP sensing plate.

Experimentation

Incidence of High energy X-ray beam line of both virgin sensing plate and CdSe-CdS core shell quantum dots (QDs) coated sensing plate using Ni filtered Cu-K\textsubscript{a} radiation (\(\lambda =1.54046\ \text{Å}\)) with a PAN analytical (X’pert-PRO) X-ray diffractometer. The electric current was detected by applying variable potential source through pico-Ameter. The forward and reverse biasing current was reading through a rheostat and shunt arrangement. The electrical properties have been studied for both single and multiple fibers at low bias voltage (0-36 V). Fibers are arranging to form a sheet material for real application purpose. Here the fiber as such taken instead of material preparation forms its melt/solution to fix the molecular orientation of fiber molecules with respect to the fiber axis. The I-V plot of the plates prepared from virgin and CdSe-CdS core shell coated fiber carried out.

Again in the next investigation, an experiment was conducted to access the X-ray based photo amplification characteristics possess, 17 KeV-ray (MoK\textsubscript{a}) allow irradiating the sample. The schematic diagram photo sensing plate with incidence of X-ray is shown in Figure 4.16. The electric current was detected by applying variable potential source through pico-Ameter. The I-V Characteristic was carried out by an in-situ analysis of X-ray (MoK\textsubscript{a}).
Fig. 4.15 Incidence of High energy X-ray beam line of both virgin sensing plate and CdSe-CdS core shell quantum dots (QDs) coated sensing plate using Ni filtered Cu-K\(_a\) radiation (\(\lambda =1.54046\) Å) with a PAN analytical (X’pert-PRO) X-ray diffractometer.

Fig. 4.16 Schematic diagram of the sample holder for Photo-detector