CHAPTER 2

CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

The characterization of materials is important for understanding their properties and applications. This chapter describes the instruments and experimental set ups utilized for various measurements towards the characterization of the synthesized CdS nanocrystals. The techniques adopted to characterize the nanoparticles are: X-ray diffraction, UV-Visible Spectroscopy, photoluminescence spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, scanning electron microscopy, transmission electron microscopy and inverted microscopy.

2.2 POWDER X-RAY DIFFRACTION (XRD)

X-ray diffraction technique is the most common and efficient method for the determination of structure and crystallinity and material identification. XRD is an apt method to examine whether a resultant material has amorphous or crystalline nature. Crystalline phases can be identified by just comparing the interplanar distance ‘d’ values obtained from XRD data with the fundamental data in Joint Committee on Powder Diffraction Standards (JCPDS).

2.2.1 Principle

X-ray diffraction is based on constructive interference of monochromatic X-rays from a crystalline sample. The X-rays, generated by a cathode ray tube are filtered to produce monochromatic radiation, collimated and directed towards the sample. X-ray primarily interact with electrons in atoms, collide and some photons from the incident beam are deflected away from original. The X-rays interfere
constructively and destructively producing a diffraction pattern on the detector. The incident X-ray radiation produces a Bragg peak if their reflections from the various planes interfered constructively. The interference is constructive, when the phase shift is a multiple of $2\pi$, this condition can be expressed by Bragg’s law [91],

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

(1)

where $n$ is an integer, $\lambda$ is the wavelength of incident wave, $d$ is the spacing between the planes in the atomic lattice and $\theta$ is the angle between the incident ray and the scattering planes. Schematic diagram of X-ray diffraction is shown in Figure 2.1.

![Figure 2.1 Bragg’s law](image)

2.2.2 Instrumentation

A typical powder X-ray diffractometer consists of a source of radiation, a monochromator to choose the wavelength, slits to adjust the shape of the beam, a sample and a detector. A goniometer is used for fine adjustment of the sample and the detector positions. The goniometer mechanism supports the sample and detector, allowing precise movement. The source X-rays contain several components; the most common being $K_a$ and $K_b$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Monochromators and filters are used to absorb the unwanted emission with wavelength $K_b$, while allowing the desired wavelength, $K_a$ to pass through. The X-ray radiation most commonly used is that emitted by copper,
whose characteristic wavelength for the K\textsubscript{a} radiation is equal to 1.5418 Å. The filtered X-rays are collimated and directed onto the sample as shown in the Figure 2.2. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of 2θ. The diffracted beam may be detected by using a moveable detector such as a Geiger counter, which is connected to a chart recorder. The counter is set to scan over a range of 2θ values at a constant angular velocity. Routinely, a 2θ range of 5 to 70 degrees is sufficient to cover the most useful part of the powder pattern. The scanning speed of the counter is usually 2θ of 2° min\(^{-1}\). A detector records and processes this X-ray signal and converts the signal to a count rate which is then fed to a device such as a printer or computer monitor. The sample must be ground to fine powder before loading it in the glass sample holder. Sample should completely occupy the square glass well. In the present work, XRD patterns were recorded using X’per PRO PANalytical and Rigaku X-ray diffractometer (RINT - 2200) with CuK\textsubscript{a} radiation at 0.02° / sec step interval.

![Figure 2.2 Schematic diagram of the diffractometer](image-url)

Figure 2.2 Schematic diagram of the diffractometer
2.3 UV - VISIBLE SPECTROSCOPY (UV - Vis)

This refers to absorption spectroscopy in the ultra-violet and visible spectral region. In this region of the electromagnetic spectrum, molecules undergo electronic transition. When sample molecules are exposed to light having an energy \( E = h\nu \) where \( E \) is energy in joules, \( h \) is Planck’s constant \( 6.62 \times 10^{-34} \text{ J s} \) and \( \nu \) is frequency in Hertz), that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength (\( \lambda \)). The optical properties of materials can be studied with the help of UV - Vis spectra.

2.3.1 Principle

The absorbance of light by molecules in the solution is based on the Beer - Lambert law, \( A = \log \frac{I_0}{I} = \varepsilon b c \), where, \( I_0 \) is the intensity of the reference beam and \( I \) is the intensity of the sample beam, \( \varepsilon \) is the molar absorptivity with units of \( \text{L mol}^{-1} \text{cm}^{-1} \), \( b \) = path length of the sample in centimeters and \( c \) = concentration given solution expressed in \( \text{mol L}^{-1} \) [92].

2.3.2 Instrumentation

The main components of the UV - Vis spectrometers are a light source, double beams (reference and sample beam), a monochromator, a detector and a recording device. The source is usually a tungsten filament lamp for visible and deuterium discharge lamp for UV measurements. The light coming out of the source is split into two beams - the reference and the sample beam as shown in the Figure 2.3. The sample and reference cells are rectangular quartz / glass containers; they contain the solution (to be tested) and pure solvent, respectively. The spectrometer records the ratio between the reference and sample beam intensities. The recorder plots the absorbance (A) against the wavelength (\( \lambda \)). The sample is prepared
into a paste and then dissolved into the solvent to make a dilute sample solution. This sample solution is filled up to mark line of the sample cell. In the present work, UV-visible absorption analyses were performed by Varian Cary 5E UV-Vis-NIR spectrophotometer and Shimadzu (Japan) 3100 PC spectrophotometer using ethanol as a dispersing medium.

**Figure 2.3 Functional Block diagram of a double beam UV-Visible Spectrophotometer**

2.4 PHOTOLUMINESCENCE SPECTROSCOPY (PL)

Photoluminescence spectroscopy is a contactless, non-destructive method to probe the electronic structure of materials. The intensity and spectral content of the emitted photoluminescence is a direct measure of various important material properties, including band gap determination, impurity levels and defect detection, recombination mechanisms.

2.4.1 Principle

Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. Photo-excitation causes electrons within a material to move into permissible excited states. These
electrons return to their equilibrium states, by a radiative process (the emission of light) or by a non-radiative process as shown in Figure 2.4. The quantity of the emitted light is related to the relative contribution of the radiative process [92].

Figure 2.4 Principle of photoluminescence

2.4.2 Instrumentation

The fluorescence instruments contain three basic items: a source of light, a sample holder and a detector. A schematic representation of a fluorimeter is shown in Figure 2.5. The light source produces light photons over a broad energy spectrum, typically ranging from 200 to 900 nm. Photons impinge on the excitation monochromator, which selectively transmits light in a narrow range centered about the specified excitation wavelength. The transmitted light passes through adjustable slits that control magnitude and resolution by further limiting the range of transmitted light. The filtered light passes into the sample cell causing fluorescent emission by fluorophors within the sample. Emitted light enters the emission monochromator, which is positioned at a 90° angle from the excitation light path to eliminate background signal and minimize noise due to stray light. Again, emitted light is transmitted in a narrow range centered about the specified emission wavelength and exits through adjustable slits, finally entering the photomultiplier tube (PMT). The signal is amplified and creates a voltage that is proportional to the measured emitted intensity. Noise in the counting process arises primarily in the PMT. Therefore,
spectral resolution and signal to noise is directly related to the selected slit widths. Sample preparation process is the same as that of UV - Visible spectroscopy. In both the cases, the sample cell (cuvette) must be free from contaminants. For the present research work, Fluorolog - 3 - 11 spectrophotometer was employed for photoluminescence measurements.

![Figure 2.5 Schematic representation of a fluorescence spectrophotometer](image)

### 2.5 FOURIER TRANSFORM INFRARED (FTIR) SPECTROCOPY

The infrared spectroscopy (IR) is one of the powerful tools for identification of compounds by matching spectrum of unknown compound with reference spectrum (finger printing), identification of functional groups in unknown substances [93]. The IR region of the electromagnetic spectrum is considered to cover the range from 50 to 12,500 cm\(^{-1}\) approximately.

#### 2.5.1 Principle

When infrared light is passed through a sample of organic compound, some frequencies are absorbed, while other frequencies are transmitted without being
absorbed. The transitions involved in the infrared absorption are associated with the vibrational changes in the molecule. Different bonds / functional groups have different vibrational frequencies and hence the presence of these bonds in a molecule can be detected by identifying this characteristic frequency as an absorption band in the infrared spectrum. The plot between transmittance against frequency is called infrared spectrum.

2.5.2 Instrumentation

Fourier transform spectrometers have recently replaced dispersive instruments for most applications due to their superior speed and sensitivity. They have greatly extended the capabilities of infrared spectroscopy and have been applied to many areas that are very difficult or nearly impossible to analyze by dispersive instruments. Instead of viewing each component frequency sequentially, as in a dispersive IR spectrometer, all frequencies are examined simultaneously in Fourier transform infrared (FTIR) spectroscopy. There are three basic spectrometer components in an FT system: radiation source, interferometer and detector. The functional block diagram of the FTIR spectrometer is shown in the Figure 2.6. The IR radiation from a broadband source is first directed into an interferometer, where it is divided and then recombined after the split beams travel different optical paths to generate constructive and destructive interference. Next, the resulting beam passes through the sample compartment and reaches to the detector. Sample preparation is very easy. Almost any solid, liquid or gas sample can be analyzed. The sample to be analyzed (minimum of 10 µg) should be ground into KBr matrix or dissolved in a suitable solvent (CCl₄ and CS₂ are preferred). Water should be removed from sample if possible. In case of solid samples, it is mixed with solid KBr (transparent in the mid-IR region), then ground and pressed. Fourier Transform Infrared measurements (FTIR) were performed using Perkin Elmer FTIR spectrophotometer by standard KBr pellet technique.
2.6 RAMAN SPECTROSCOPY

Raman spectroscopy is a method of determining modes of molecular vibrations [94]. It is predominantly applicable to qualitative and quantitative analyses of covalently bonded molecules used to distinguish between different phases of the same material and can provide information on strain and periodicity in modulated structures. It is used extensively to characterize semiconductor surfaces.

2.6.1 Principle

Raman signal occurs due to the ‘change in polarizability’ of a molecule. This is a measure of the deformability of a bond in an electric field. The Raman effect is not an absorption effect like infrared, but depends on the polarizability of the vibrating group.

2.6.2 Instrumentation

A Raman system typically consists of four major components: Excitation source (Laser), Sample illumination system and light collection optics, Wavelength selector (Filter or Spectrophotometer), Detector (Photodiode array, CCD or PMT). A schematic diagram of the Raman spectrophotometer is shown in Figure 2.7. The sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample. Raman spectra are obtained from bulk solids, liquids, tablets, polymers, paper, etc. Sample preparations, such as grinding can also lead to changes in solid states (e.g. hydration state, polymorphism, hydrogen bonding), which sometimes have an impact on the final detection method. Raman analysis requires virtually no
sample preparation and thus provides significant cost savings. In the present work, Raman spectra were obtained using JASCO NR 1800 Raman spectrophotometer equipped with Nd: YAG laser.

\[ \text{Figure 2.7 Schematic diagram of a Raman spectrometer} \]

2.7 SCANNING ELECTRON MICROSCOPE (SEM)

2.7.1 Principle

The scanning electron microscope (SEM) is a very useful imaging technique that utilized a beam of electrons to acquire high magnification images of specimens. The SEM maps the reflected electrons and allows imaging of thick (~ mm) samples. SEM images are formed by rastering (scanning) a beam across the sample and forming the image point - by - point [95].

2.7.2 Instrumentation

The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. A schematic diagram of the SEM is shown in Figure 2.8. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X - rays are ejected from the sample. Detectors collect these
X-rays, backscattered electrons and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image. In this research work, the powder samples were placed on the carbon tape which was attached to the sample holder. JEOL JSM 6320F (FESEM), F E I Quanta FEG 200 (HRSEM) were used to study the surface morphology of the sample.

![Figure 2.8 Schematic diagram of a Scanning Electron Microscope](image)

### 2.8 TRANSMISSION ELECTRON MICROSCOPE (TEM)

Transmission Electron Microscopy is an effective direct observation method to view the atomic and molecular arrangement. TEM is an effective probe to study the size and shape of nanoparticles. The crystallinity and size of the particles can also be determined from TEM analysis.

#### 2.8.1 Principle

In this form of microscopy, a beam of electrons transmits through an extremely thin specimen, and then interacts with the specimen when passing through it [96]. The sample must be thin enough to transmit sufficient electrons such that enough intensity falls on the screen to give an image.
2.8.2 Instrumentation

TEM contains four parts: electron source, electromagnetic lens system, sample holder and imaging system as shown in Figure 2.9. The electron beam coming from the source is tightly focused by the electromagnetic lenses and the metal apertures. The system only allows electrons within a small energy range to pass through, so the electrons in the electron beam will have a well-defined energy. This beam falls on the sample placed in the holder. The electron beam passes through the sample. The transmitted beam replicates the patterns on the sample. This transmitted beam is projected onto a phosphor screen. In the present work, TEM images were recorded by JEOL JEM 2100F transmission electron microscope at an accelerating voltage of 200 kV. To obtain the images, the powder samples were dispersed in ethanol and it was ultrasonicated for 20 minutes. A drop of dispersion was coated onto the copper grid and TEM images were obtained.

![Figure 2.9 Schematic diagram of a Transmission Electron Microscope](image-url)
2.9 INVERTED MICROSCOPE

Microscopes come in two basic configurations: upright and inverted. An upright microscope has the illumination system (light) below the stage and the lens system above the stage. An inverted microscope has the illumination system above the stage and the lens system below the stage. Inverted microscopes are better for looking through thick specimens, such as dishes of cultured cells, because the lenses can get closer to the bottom of the dish, where the cells grow. The inverted microscope is useful due to its ability to maintain a more natural environment for the specimen, thus extending its life. The viewing of valuable life processes can be researched longer. This is its major advantage over a compound light microscope. Leica DM IL LED inverted microscope was employed for recording the images of cultured cells.

Figure 2.10. Schematic diagram of an inverted microscope
2.9.1 **Instrumentation**

The inverted microscope has similar components to that of a compound microscope: Illumination system (light source, tungsten - filament light bulbs), lenses (the ocular lens and objective lens), Specimen control (stage), condenser. Figure 2.10 illustrates the components of the inverted microscope.

**Illumination system**

A powerful 6 volt, 30 watt halogen bulb with pre - centered socket provides enhanced image quality and brightness for the observation of specimens.

**Condenser**

The standard condenser has a working distance of 73 mm. The condenser is an important device as it controls the amount of light falling on the sample. This influences the visualization of the sample.

**Stage**

A mechanical stage with 112 mm (X) by 72 mm (Y) movement, drop - down coaxial controls and plate holder is attached, depending on model. Slide, chamber and petri dish holding plates of various sizes are available separately.

**Lenses**

The objective lenses are near the stage on the revolving nosepiece. The objective is set with its front element uppermost and the eyepieces are angled upward so that the observer can study specimens that are still in their watery medium.

**Viewing heads**

The eyetubes inclined at 30 degrees with the left eyetube having graduated dioptrier settings. The interpupillary distance on the viewing heads is adjustable.
2.10 CONCLUSION

The basic principles of characterization techniques, such as X-ray diffraction, UV-Visible spectroscopy, Photoluminescence spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, Scanning electron microscopy, Transmission electron microscopy and inverted microscopy are discussed.