2
Experimental Methods and Instrumentation

This chapter describes the basic principle of the synthesis procedure of semiconducting QDs. Mainly a brief discussion about the hot injection method for metal chalcogenide QDs and thermal reduction of $(NH_4)_2MS_4$ (M=Mo, W, etc.) under an inert atmosphere for MS_2 QDs has been presented in the current chapter. Furthermore, the basic working principle of different material characterization techniques such as XRD, XPS, UPS, TEM, SEM, absorption spectroscopy, fluorescence spectroscopy, AFM and STM will be discussed. In addition, the device fabrication process and electrical characterization technique used in this work will also be discussed in the present chapter.

2.1 Synthesis of Materials and Device Fabrication

In this work, semiconducting CdSe QDs have been prepared using the hot injection method, while MoS_2 QDs have been prepared using thermal reduction of $(NH_4)_2MoS_4$ in the presence of a reducing agent such as oleylamine (OAM) under an inert environment. The prepared QDs are blended with a polymer named poly (4-vinyl pyridine) (PVP) for use in the active layer of the device. The devices have been fabricated by spin coat method on ITO coated glass and pre-patterned electrode on glass substrates followed by metal electrodes deposition in a thermal evaporation unit.

2.1.1 Hot Injection Method for the Synthesis of Semiconducting QDs

The hot injection method is widely used for the synthesis of high-quality monodisperse metal-chalcogenide QDs such as PbS QD, CdSe QD, CdTe QD etc. and other semiconducting QDs such as halide perovskite QDs. In this method, metal (Pb, Cd, Zn etc.) precursor is added to the required amount of ODE and loaded in a three-neck flask. For encapsulating the QDs, different capping agents such as OA, OLA, TOPO, DDT etc., are added to the ODE solution. The reaction flask containing metal precursor, ODE and capping agents is then evacuated under vacuum using a standard Schlenk line. The reaction bath is then heated under a vacuum to remove any moisture from the reaction mixture for a sufficient time. Then the reaction bath is purged with some inert gas such as N_2 or Ar. After switching the Ar or N_2 atmosphere, the metal precursor is totally dissolved in the solution and a transparent clear solution of metal-oleate is formed. Then the reaction temperature is increased to the desired value. Meanwhile, the chalcogenide (S, Se and Te) precursor is prepared and fully dissolved in ODE to obtain a clear homogeneous solution. When the reaction temperature reached the desired value and became stable, a certain amount of the chalcogenide precursor solution was quickly injected into the metal-oleate solution in the reaction flask. The schematic illustration of the hot injection method is shown in Figure 2.1. The color of the mixed solution may change immediately after injection, or it may be changed after a few minutes depending upon the growth of the QDs. The heat source is switched off immediately after injection, or the injection temperature is maintained for a few minutes for the growth of the particles and then the reaction is quenched by immersing the reaction flask in an ice-water bath, depending upon the nature of QDs. When the reaction bath is cooled to room temperature (RT), some anti-solvents such as acetone, ethanol or methanol are mixed with a crude solution to precipitate the QDs from the solution. The QDs are separated by centrifuging the solution at a specific rpm and collected by removing the upper transparent part. The collected QDs then dispersed in some nonpolar solvent such as toluene, octane, hexane etc. The cleaning procedure

of QDs is repeated several times to get the final QDs powder. The Schlenk line setup for the synthesis of QDs and centrifuge setup for separating the QDs from crude solution have been shown in Figure 2.2.

The size of the QDs depends upon several parameters such as injection temperature, reaction time, amount of capping ligands used, amount of ODE etc. For monodisperse QDs, controlled and homogeneous nucleation is needed. If all of the particles nucleate at once, the growth will be uniform which results in monodisperse QDs. On the other hand, if the nucleation occurs randomly during the crystallization process, the growth will be different for different particles, which results in QDs of different sizes. If the injection temperature increases, particle size increases. For desired particle size growth process should be terminated. The growth of the particles is terminated by cooling the reaction bath. Sometimes the growth is stopped by immersing the reaction bath in an ice-water bath. For the synthesis of monodispersed QDs of the desired size, controlled nucleation and growth with optimized parameters are highly needed in the hot-injection method.

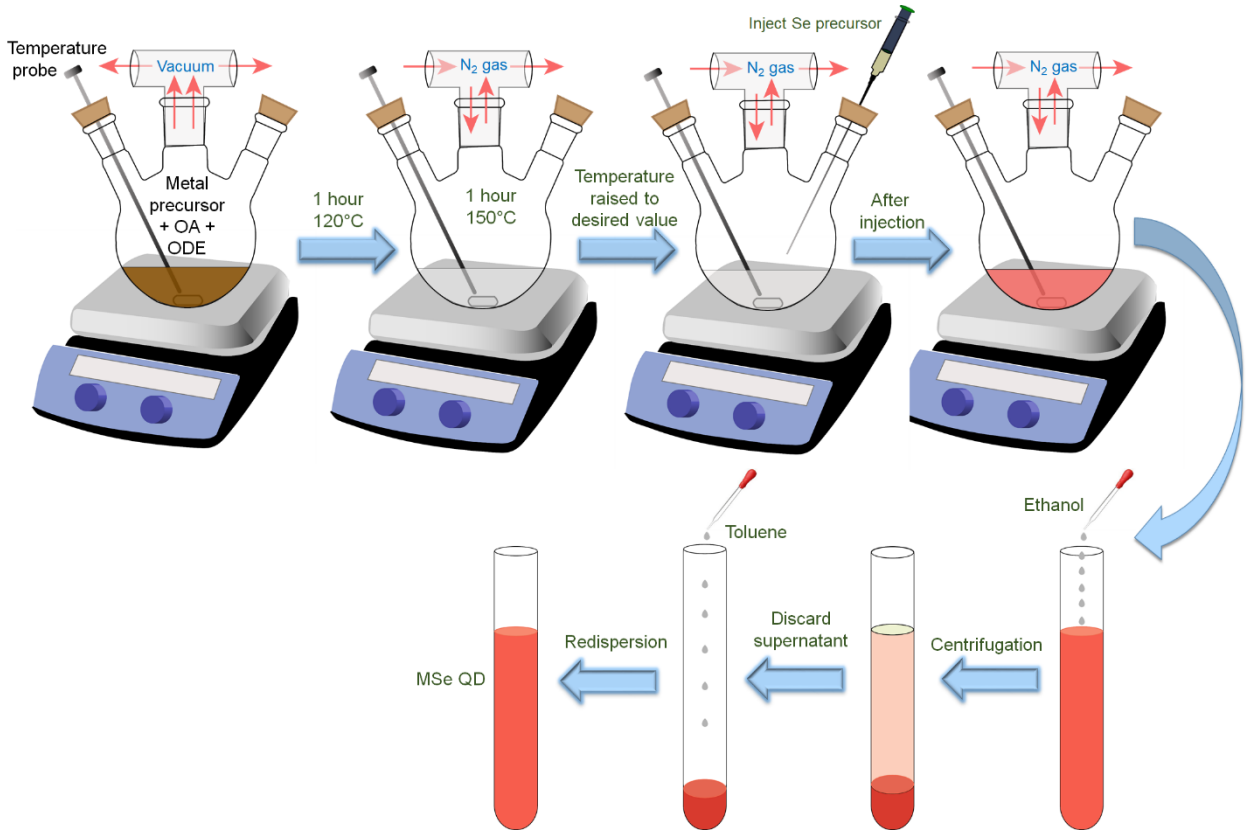

Figure 2.1: Schematic illustration of the synthesis procedure of semiconducting MSe (M = Cd, Pb etc.) QDs

2.1.2 Thermal Reduction of $(NH_4)_2MoS_4$ for MS_2 (M= Mo and W) QDs

For the synthesis of transition metal di-chalcogenides (TMDCs) QDs such as MoS_2 and WS_2 QDs, solvothermal synthesis and ultrasonication-assisted exfoliation of bulk TMDCs powder is generally used [Dong et al., 2016; Ren et al., 2015; Yin et al., 2020]. Another type of bottom-up chemical synthesis was described for MoS_2 and WS_2 QDs by Zhang et al. using the method of thermal reduction of a single source in the presence of a reducing agent [Lin et al., 2015a]. In this method, $(NH_4)_2MoS_4$ (for MoS_2 QDs) or $(NH_4)_2WS_4$ (for WS_2 QDs) is used as a precursor. Upon heating in an inert atmosphere, $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$ are thermally decomposed and then reduced to MoS_2 and WS_2, respectively, in the presence of a reducing agent such as oleyl amine (OAM). The OAM is not only used as a reducing agent but also as a capping agent for QDs. We have synthesized MoS_2 QDs using thermal reduction of $(NH_4)_2MoS_4$. In this process, first, a mixture of $(NH_4)_2MoS_4$, OA and OAM in ODE is loaded in a three-neck flask. Then the reaction

flask is degassed under vacuum by heating at 120 °C for 2.5 hours to remove any moisture from the reaction flask. Then the reaction flask is purged with dry N_2 using a standard Schlenk line and the temperature is gradually increased upto 250 °C. At this temperature, the reaction mixture is kept for 3 hours. Then the heater is switched off. When the reaction bath is cooled to RT, acetone is added to the crude solution. Then the crude solution was taken into test tubes and acetone was added to the crude solution to precipitate the QDs. The solution is then centrifuged and the precipitated black MoS_2 QDs are collected by removing the upper transparent supernatant. The MoS_2 QDs are then redispersed in chloroform. This process is repeated several times to remove excess OA, OAM and other unreacted products. The MoS_2 QDs are finally dispersed in chloroform for future use. The size of the QDs is dependent on the reaction temperature, time and amount of reducing agent used. The size of quantum dots increases with increased reaction temperature and time. If the amount of OAM is increased, bigger QDs are produced. The schematic of the synthesis process is shown in Figure 2.3. The Schlenk line and centrifuge setup used in our work are shown in Figure 2.2.

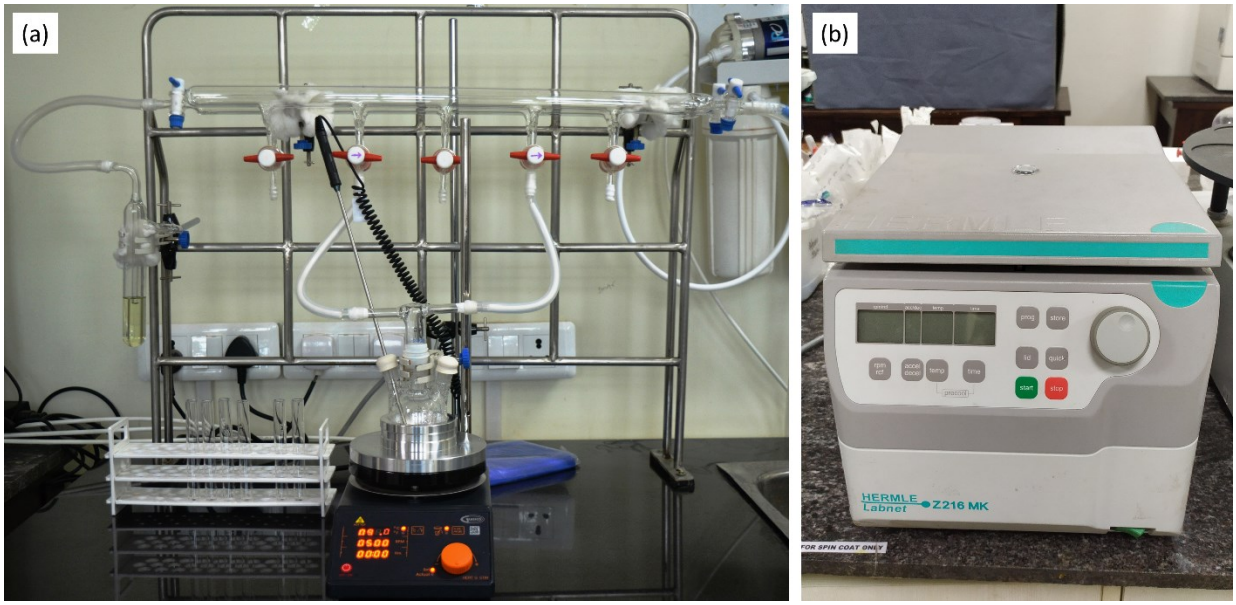

Figure 2.2: The photograph of (a) the Schlenk line setup and (b) centrifuge setup

2.1.3 Device Fabrication Technique

The resistive memory device fabrication process using QDs-PVP composites is mainly a 3-step process and is to be carried out with care. First, the middle of the ITO substrates is covered with tape and the ITO in the two side regions is etched using zinc dust and hydrochloric acid. After removing the tape, an ITO strip will be formed in the middle part of the substrate. The etched substrates are then cleaned by ultrasonication sequentially in a soap solution, deionized water (DI), acetone, DI, methanol, and DI for 15 min each. Then the cleaned substrates are dried with an N_2 gun and ready for use. In another fabrication process, glass substrates were first cleaned by ultrasonication sequentially in a soap solution, deionized water (DI), acetone, DI, methanol, and DI for 15 min each, followed by drying in an N_2 gun. Then Al metal electrodes are deposited onto the cleaned glass substrate using a metal shadow mask in a thermal evaporation unit under a high vacuum for the bottom electrodes pattern. The active layer of the device is prepared by blending the QDs with PVP polymer. The mixture of QDs-PVP is then ultrasonicated for 1 hour for a homogenous solution. If the mixture is not homogenous, the deposited film will not be smooth. To deposit the active layer, the QDs-PVP composite solution is coated on the cleaned substrates using a spin coater at a certain rpm. In this method, the substrate is first covered with solution and then spun at a certain rpm as shown in Figure 2.4a. The Figure 2.4b shows a photograph of a commercial spin coater. The thickness and smoothness of the thin film depend upon the spinning rpm, acceleration and the adhesion of the solution with the substrate.

For a better-quality thin film, the adhesion of the solution with the substrate should be good. To confirm the proper adhesion, the substrate should be cleaned carefully. Any organic residues present on the substrate can degrade the film quality. The spin-coated film is then heated at 80 °C for 30 min in a hotplate for complete removal of the solvent. Then the coated film on the substrates is transferred to a thermal deposition unit for top electrode deposition. Metal top electrodes of desired thickness are deposited using a metal shadow mask under a high vacuum in the thermal deposition unit.

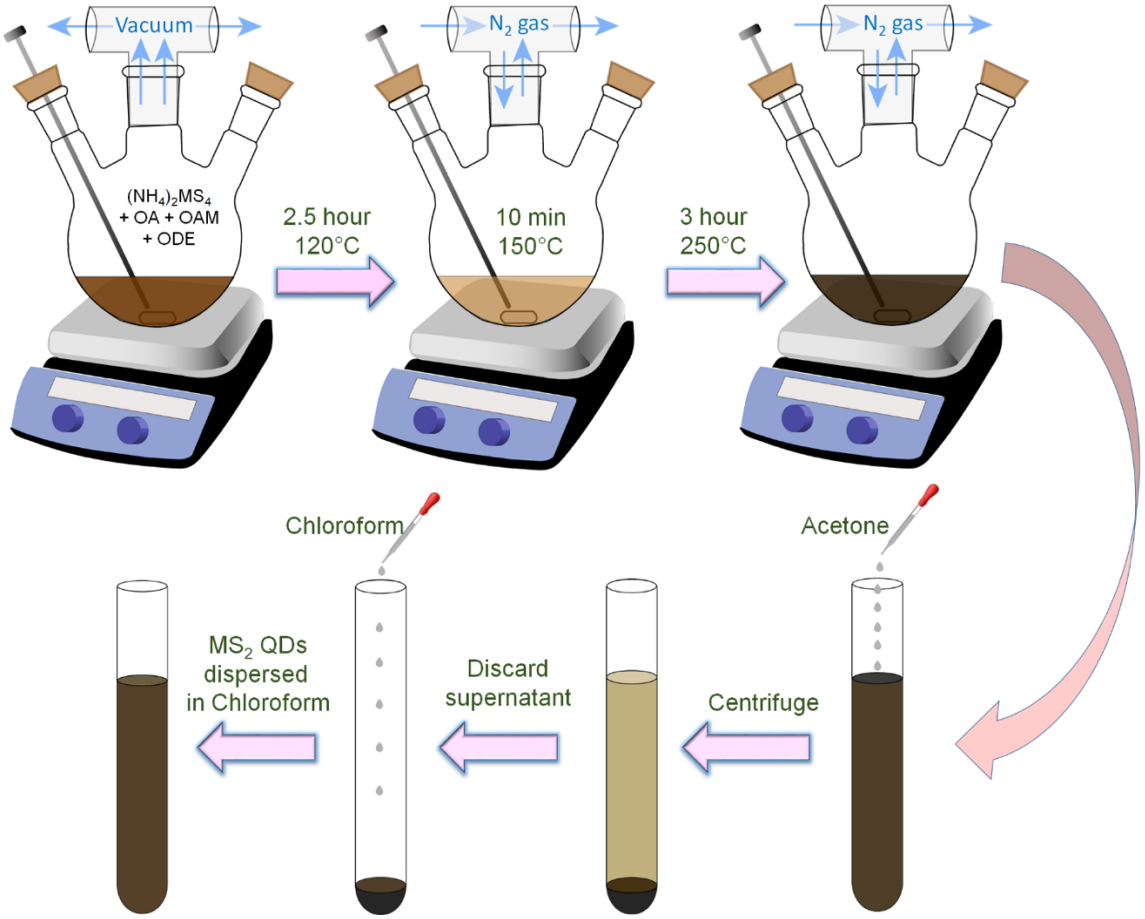

Figure 2.3: Schematic of the synthesis procedure of MS_2 (M = Mo and W) QDs

2.2 Characterization Techniques

For materials characterization, XRD, XPS, TEM, SEM, UPS, AFM, STM, absorption spectroscopy and fluorescence spectroscopy have been used. For electrical characterization, two probe system in association with Keithley 6430 sourcemeter has been used.

2.2.1 X-ray Diffraction (XRD)

XRD is a powerful non-destructive technique used to analyze the crystallographic information of poly and single crystalline materials. This technique gives useful information, including crystal structure, crystal phase, lattice parameters, lattice spacing, average crystallite size, orientation lattice planes, and crystallinity of crystalline materials. The basic working principle of XRD is based on Bragg's law of diffraction, which is expressed as: $2d_{hkl}sin\theta = m\lambda$, where d_{hkl} is the spacing between lattice planes, θ is the incident angle, m is the order of the diffraction and λ is the wavelength of the incident X-ray beam. The monochromatic X-ray beams get scattered when they interact with a crystalline sample. The scattered X-rays interact with each other constructively and destructively, and this phenomenon is called X-ray diffraction as shown in Figure 2.5a. The powder XRD instrument has mainly three parts which include the X-ray source, sample region and detector region, as shown in Figure 2.5b. The source of X-rays is an X-

ray tube in which the electrons emitted from hot tungsten filament are accelerated by the application of a high voltage and hit the metal target such as Cu and Mo to produce X-rays. Then the X-rays are focused on the sample at a particular incident angle which is placed on a specific sample holder. The diffracted X-rays from the sample are then collected by the detector by rotating the detector at a different angle. Sometimes, the angle of the source and the detector are varied to collect the data. The image of the XRD instrument used in this work is shown in Figure 2.5c.

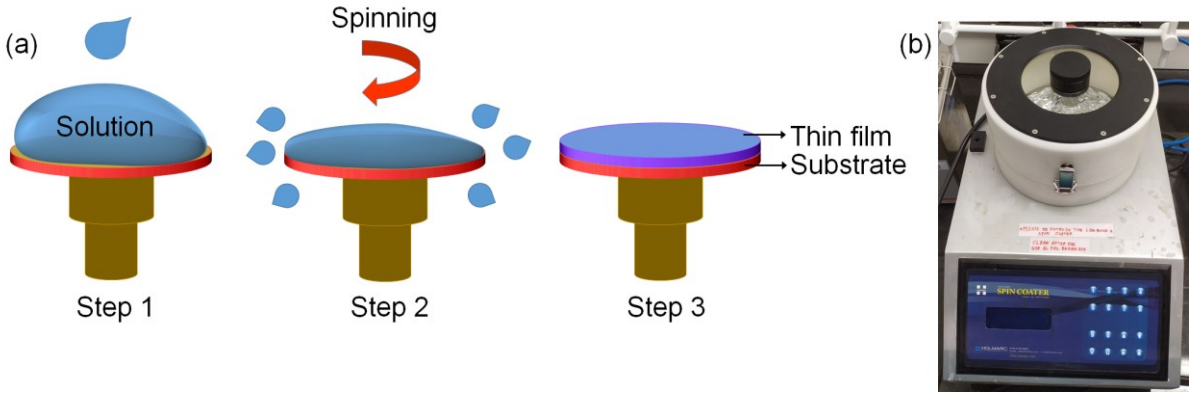

Figure 2.4: Schematic of the (a) spin coating process and (b) photograph of the spin coater

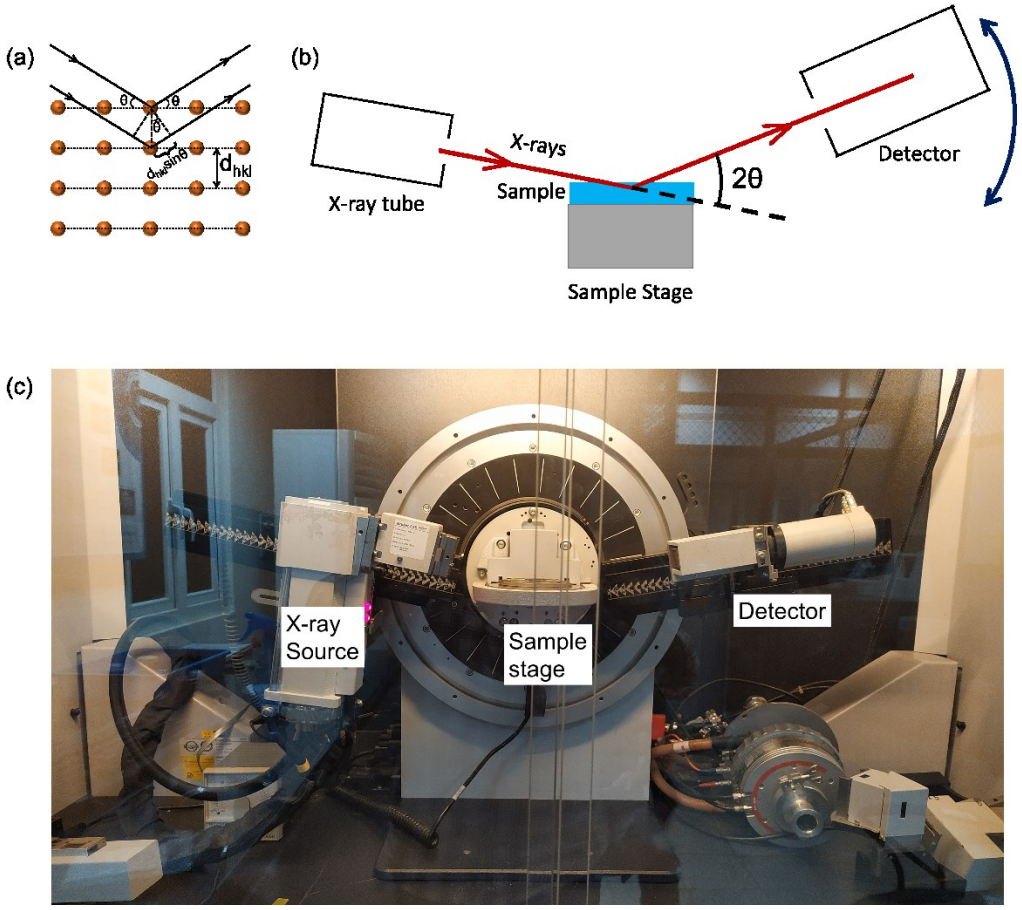

Figure 2.5: Schematic of the (a) X-ray diffraction in lattice plane, (b) working principle of an X-ray diffractometer and (c) photograph of a commercial X-ray diffractometer

2.2.2 X-ray Photoelectron Spectroscopy (XPS)

XPS is a useful technique for the elemental analysis of a material. The basic principle of XPS is similar to the photoelectric effect, but instead of the light photon, the X-ray photon is used in XPS to eject electrons from the material's surface. When an X-ray photon with sufficient energy

is incident on a material, an electron from the inner shell of the atom is knocked out and ejected from the surface, as shown in Figure 2.6a. This ejected electron is called as X-ray photoelectron. The photoelectrons have the kinetic energy $E_K = h\nu - E_b - \Phi$, where h is Planck's constant, ν is the frequency of the incident X-ray photon, E_b is the binding energy and Φ is the required energy for an electron to escape from the surface of the material. The value of Φ depends on the properties of the material. The binding energy of atomic electrons has characteristic values. As these values are unique for every element, they are used to identify the elements present in the materials. From the characteristic peaks of the X-ray photoelectrons intensity vs binding energy spectra, the elements present in a material can be easily identified. Sometimes, an XPS spectrum contains peaks generated from Auger electrons. When a high-energy X-ray photon knocks out an electron in the inner shell, the atom is excited and becomes ionized. To return to the normal state, an electron from an outer shell fills the vacancy in the inner shell. The energy difference between the inner and outer shell is then released either in the form of an Auger electron or characteristic X-ray photon. The production of Auger electrons is shown in Figure 2.6b. Always an ultrahigh vacuum (10^{-8} – 10^{-10} mbar) is needed for XPS. This is because the photoelectrons are easily scattered by the gas molecules and are hard to reach the detector. The scattering will reduce the peak intensity and also increase the background noise in the spectrum. An XPS instrument consists of mainly four parts which are an X-ray gun, electrostatic lenses, hemispherical analyzer and detector, as shown in Figure 2.6c. The X-ray gun produces high-energy X-ray photons which are focused on the sample. Photoelectrons generated from the sample are then focused by electrostatic transfer lenses to reach the entrance slit of the hemispherical analyzer. The hemispherical analyzer consists of two concentric hemispheres with different radii. Different voltages are applied in the inner and outer hemispheres so that a median equipotential surface will be generated inside the analyzer. An entrance slit allows the photoelectrons to enter the hemispherical analyzer. On the other end, an exit slit allows the electrons to reach the detector from the hemispherical analyzer. The hemispherical analyzer allows only the electrons with particular energy called pass energy. The allowed electrons are injected tangentially to the median equipotential surface and reach the detector. The detector collects the photoelectrons and the plot of photoelectron intensity vs binding energy is generated by post processing techniques.

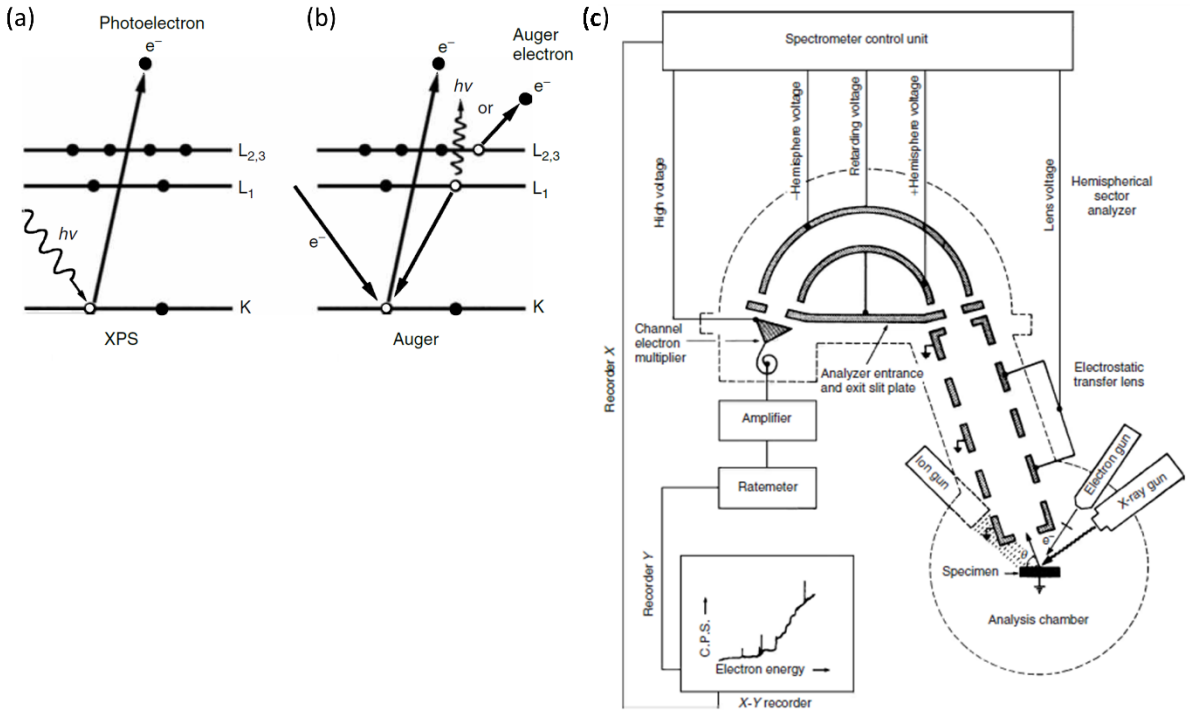

Figure 2.6: Schematic of the generation of (a) X-ray photoelectron, (b) Auger electron [Leng, 2009] and (c) schematic diagram of XPS instrument (Watts 1990).

2.2.3 Ultraviolet Photoelectron Spectroscopy (UPS)

The basic working principle of ultraviolet photoelectron spectroscopy is similar to that of XPS. Instead of X-rays, ultraviolet photons are bombarded on the sample to produce photoelectrons. The photons used in the UPS have much lower energy than that are used in XPS. The UPS technique is used to determine the molecular orbital energy in the valance region. The source of ultraviolet photons is generally a gas discharge lamp. The gas discharge lamp is filled with helium gas. The emitted photons from helium-filled gas discharge lamps have energies of 21.2 eV (He I) and 40.8 eV (He II). As the photons which have lower energies are used in UPS, it gives the spectral information of the valance band region. The valance band position and the information of work function can be measured from UPS spectra. To determine the work function, the difference between the fermi level and the cut-off tail of the low kinetic energy end of the spectrum is measured and subtracted from the incident photon energy. A small bias to the surface of the sample is applied during the measurement of the work function.

2.2.4 Scanning Electron Microscopy (SEM)

The SEM is used for imaging the morphology, texture and structure of the sample. A focused high-energy electron beam is generated in SEM and when this high-energy electron beam interacts with the sample, the sample-electron beam interaction gives various information such as morphology, texture, chemical composition, and crystalline structure of the sample. When a high-energy electron beam is incident on a sample, various phenomena can occur. The electron-sample interaction produces secondary electrons, Auger electrons, backscattered electrons, diffracted back scattered electrons, characteristic X-rays, continuum X-rays and fluorescent X-rays depending upon the interaction volume of the sample. The schematic of the type of signals produced upon electron-sample interaction has been shown in Figure 2.7. The secondary electrons give information about the topography and morphology of the sample and are therefore used for imaging in SEM. The backscattered electrons are used for determining the compositional contrast in multiphase samples. The produced X-ray is used for determining the elemental mapping of the sample. The basic structure of an SEM instrument is shown in Figure 2.8a. SEM consists of an electron gun, a few electromagnetic lenses and apertures, and detectors. The electron gun produces electrons because of thermionic emission from the filament. The filament is usually a tungsten filament. In modern SEM, field emission technology is used for high beam brightness and clarity. In field emission SEM (FESEM), electrons are generated by applying a very high electric field to a metal surface. The injected electrons from the filament are accelerated by applying high voltage to produce a high-energy electron beam. A high vacuum is needed to avoid any interaction of electron beam with gas molecules. The energy of the electron beam is typically in the range of 1 KeV to 40 KeV. The high-energy electron beam is then focused with the help of two electromagnetic lenses and apertures. Then the focused electron beam is passed through a pair of scanning coils which deflects the beam in x and y directions for a raster scan in a rectangular area on the sample. After passing through the scanning coils and objective lens, the electron beam is passed through a final aperture and incident on the sample. After the electron beam-sample interaction, the secondary electrons are collected by the secondary electron detector. The backscattered electrons are collected by a backscattered electron detector. The emitted X-rays are analyzed for energy dispersive spectroscopy (EDS). The photograph of a commercial FESEM is shown in Figure 2.8b. The surface of the samples is coated with conducting elements such as gold or carbon for use in SEM to avoid an accumulation of electrons on the sample. With continuous imaging, the electrons are accumulated on the sample surface and these accumulated electrons can repeal the new electrons from the electron gun, which results in hazy images.

2.2.5 Transmission Electron Microscopy (TEM)

TEM is a powerful technique for imaging on the atomic scale and determining the atomic arrangement. This technique also uses high-energy electrons beam like SEM, but here electron beam is transmitted through a very thin sample (thickness around 100 nm) and the transmitted

electrons are then focused and projected on a fluorescent screen to produce the image. For the transmission of electrons through the sample, the sample should be very thin and special care should be taken during sample preparation in TEM. The TEM produces a high-resolution image of crystal planes, lattice spacing, atomic arrangement, grain boundaries, twin boundaries, crystal defects etc. TEM has much higher magnification and resolution than SEM. The operating principle of a TEM is quite similar to that of an optical microscope, except that TEM uses high-energy electrons beam instead of light for imaging. The schematic of the basic structure of a TEM is shown in Figure 2.9a. The electrons are emitted by an electron gun. There are basically two types of electron guns used in the TEM, which are thermionic emission guns and field emission guns. In thermionic emission guns, generally, tungsten or lanthanum hexaboride filament as a cathode is used. The filament is heated to a high temperature by passing a current through it. Because of the high temperature, the kinetic energy of the electrons overcomes the surface energy barrier, which enables the conduction electrons to leave the surface. In a field emission gun, no thermal energy is needed for electron emission. Electrons are extracted by applying a high voltage to the metal surface. A tunneling process instead of thermionic emission makes the electrons cross the surface barrier. The electrons emitted from the electron gun are then accelerated by a high voltage to produce a high-energy electron beam. The energy of the electron determines its wavelength and wavelength significantly determines the resolution of the image. Higher acceleration voltage reduces the wavelength of the electrons and hence gives better resolution. A high vacuum is needed to avoid any interaction of electron beam with the gas molecules. The high-energy electron beam is then focused by an electromagnetic condenser lens. In an optical microscope, optical lenses made of glass are used to focus the light. But electron microscope electromagnets are used as a lens to focus the high-energy electron beam. The focused beam then passes through a condenser aperture and is incident on the sample. After passing through the sample, the transmitted electrons are focused using an objective electromagnetic lens and passed through the objective aperture. After passing through the objective aperture, the transmitted electrons are projected on a fluorescent screen using a projector electromagnetic lens. The magnified and high-resolution image of the sample is produced on the screen. The photograph of a commercial TEM is shown in Figure 2.9b. Preparation of samples is one of the most challenging steps in TEM. The sample should be electronically transparent and therefore, the thickness of the sample should not be more than 100 nm. In this work, TEM is used for the high resolution and magnified images of individual QDs. For sample preparation, QDs dispersed in toluene or chloroform are drop cast on the TEM grid made of copper mesh, which is used in this work.

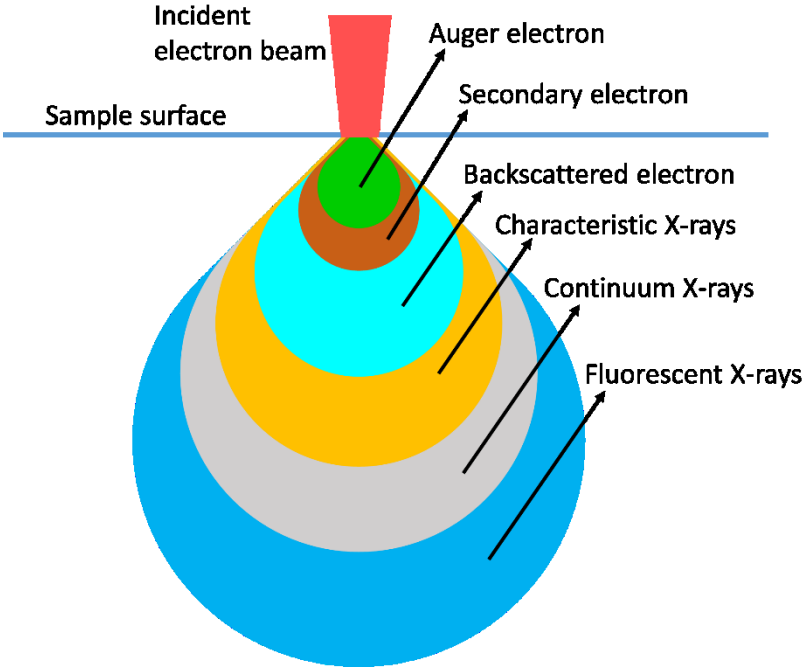

Figure 2.7: Schematic of the generation of different types of signals by electron-sample interaction

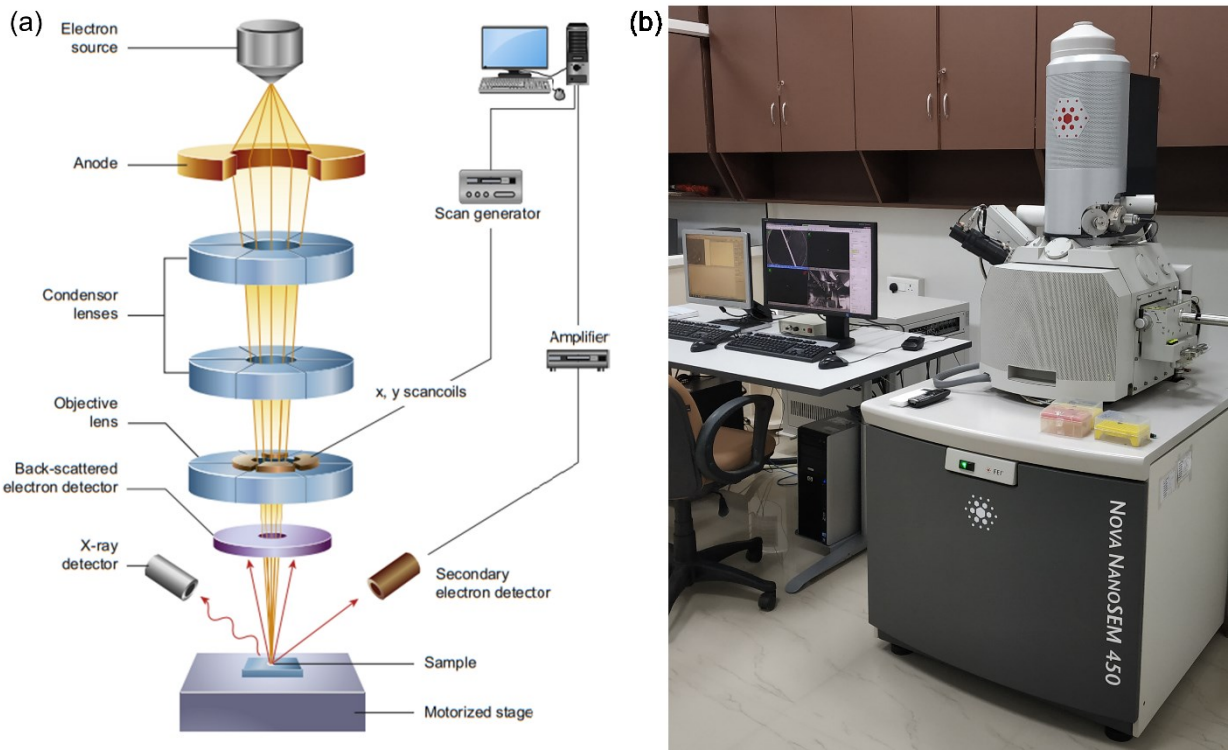

Figure 2.8: (a) Schematic diagram of the working principle of SEM [Inkson, 2016] and (b) photograph of a commercial FESEM

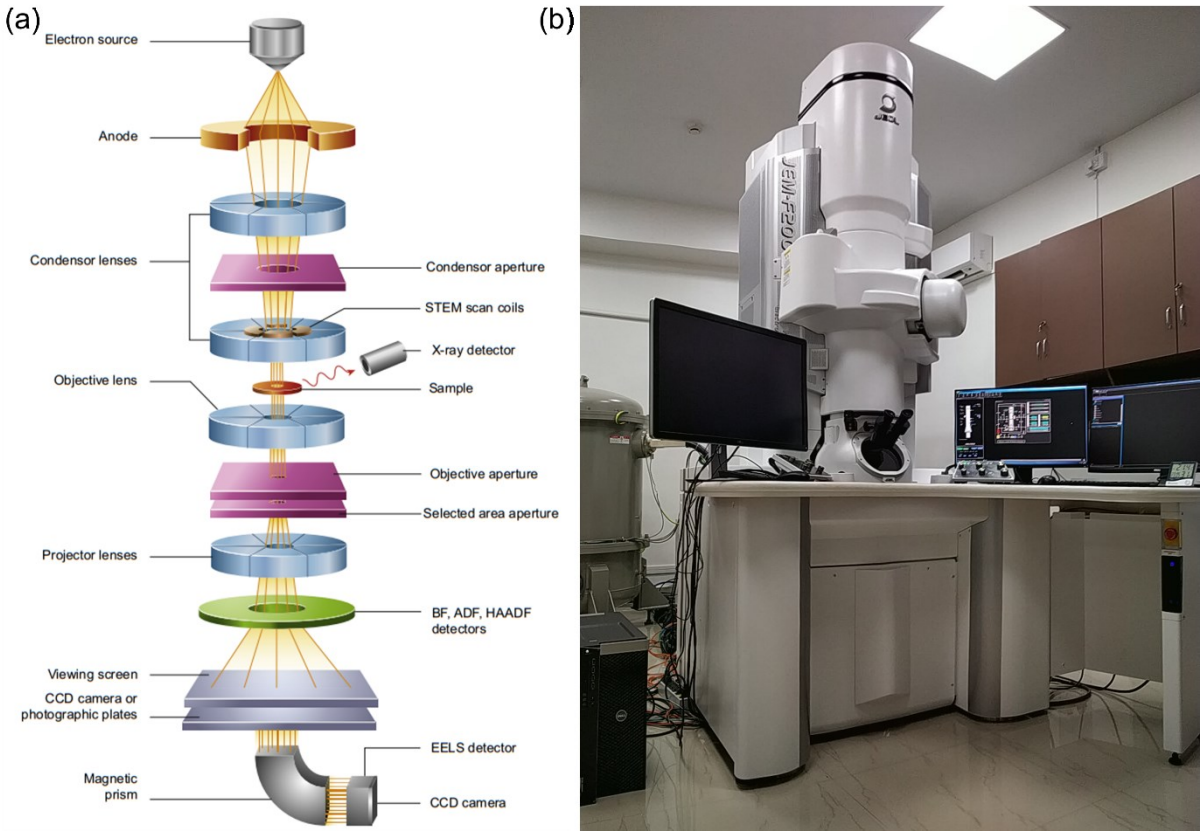

Figure 2.9: (a) Schematic diagram of the working principle of TEM [Inkson, 2016] and (b) photograph of a commercial TEM

2.2.6 Atomic Force Microscopy (AFM)

AFM is one type of scanning probe microscopy for imaging the surface morphology and surface roughness of a sample. AFM uses a sharp tip for scanning to probe the surface topography. The tip is attached to a cantilever. When the tip approaches very close to the surface of the sample, the tip and cantilever deflect. A laser beam detects the deflection caused by the tip movement away and towards the surface depending upon the surface topology. By reflecting the incident laser beam on the flat top surface of the cantilever and the change in the direction of the reflected beam caused by the deflection of the cantilever is detected by a position-sensitive photodiode (PSPD). As the tip scans the surface of a specific area in a raster way, the cantilever deflects according to the topology of the surface. The deflection of the cantilever is recorded by tracking the change in a reflected laser beam by the photodiode and a topography image of the surface is generated. In AFM, a three-dimension image of the surface can be determined. A feedback loop is used to control the distance of the tip to the surface and control the laser position as shown in Figure 2.10a. The operation mode of the AFM is three types. They are noncontact mode, contact mode and tapping mode. There are two types of cantilever tips used in the AFM. One is a single beam and another is a triangular beam cantilever. The single beam cantilever is made of silicon. The triangular beam cantilever is made of silicon nitride. The lateral resolution of the AFM depends on the apex of the tip and the opening angle of the tip. The photograph of a commercial AFM instrument are shown in Figure 2.10b-c.

2.2.7 Scanning Tunneling Microscopy (STM)

STM is a very powerful scanning probe microscopy technique to determine the surface topography of a sample in atomic resolution. The working principle of STM relies on the quantum mechanical tunneling effect. STM also uses a sharp tip, but unlike AFM, the tip is conducting in STM. When the tip approaches the sample such that the gap between sample and tip is on the atomic scale, there is a potential barrier. In quantum mechanics, there is a finite probability that the electrons having less energy than the potential barrier can tunnel through the potential barrier. This phenomenon is called quantum mechanical tunneling. If a small bias is applied between tip and sample, the electrons from the tip or sample can tunnel through the potential barrier between tip and sample. This gives rise to a tunneling current which can be expressed as $I_t = V_b \exp(-Cd)$, where V_b is the applied bias, d is the distance between tip and sample and C is a constant which depends on the nature of the materials. The working principle of STM is shown in Figure 2.11a. The tunneling current is related to the local density of states (LDOS) near the Fermi level of the sample. The LDOS at the Fermi level is important in the tunneling process. LDOS determines the number of participating electrons in the tunneling process. A piezoelectric scanner is used for scanning a specific area of interest with a raster type of scanning. By measuring and setting the value of the tunneling current and using a feedback loop, the motion of the piezoelectric scanner is controlled precisely. The output signal from the piezoelectric scanner is converted into an electrical signal and amplified to produce a three-dimensional image of the surface. The STM can scan in constant current mode in which the tunneling current is set to a specific value and kept constant. The piezoelectric scanner moves up and down according to the topography of the surface and the movement is recorded and converted to an electrical signal to produce an image. Or, the STM can be operated in constant height mode, in which the tip is kept at a constant height and the tunneling current is measured according to the topography of the surface. In this mode, the feedback loop is turned off and the sample should be atomically smooth without having any tilt, otherwise, the tip may be crashed during scanning. There is another operating mode in STM which is known as atom manipulation mode. In atom manipulation mode, an atom is relocated or removed from the surface. In this mode, an adatom is transferred from the surface to the tip and then placed in another location on the surface. The attaching and releasing of the atom to and from the tip are controlled by voltage pulses.

A sharp tip is prepared by electrochemically etching of tungsten or Pt-Ir alloy wire. STM can work in the air, but an oxide layer formed on the conducting sample surface prevents the tunneling process. Therefore, most of the STM measurements are carried out in an ultrahigh

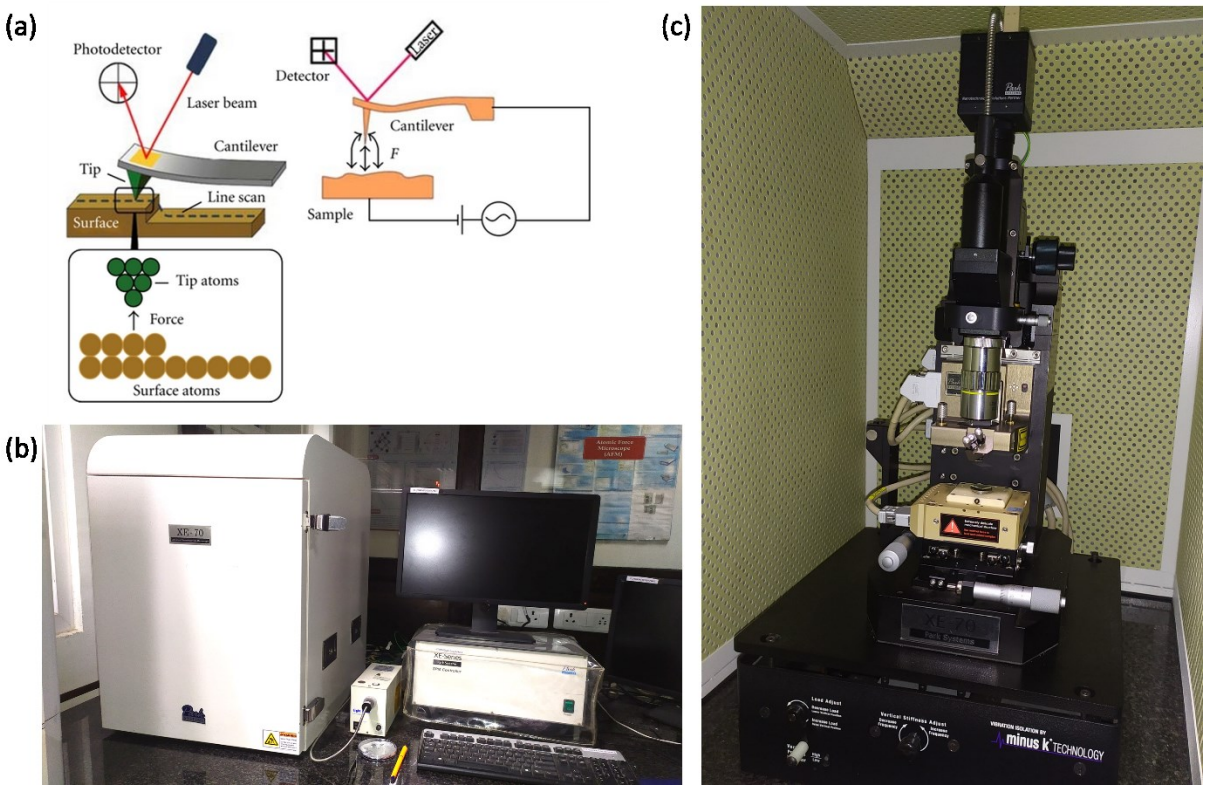

Figure 2.10: (a) Schematic diagram of the working principle of AFM [Ali, 2012] and (b) - (c) photographs of a commercial AFM

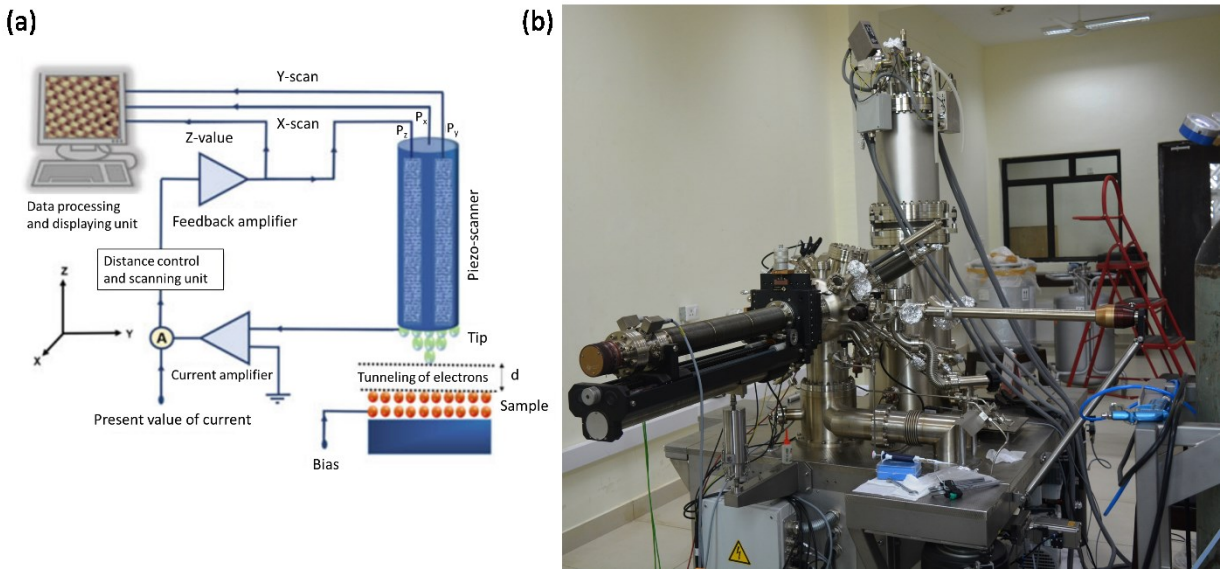

Figure 2.11: (a) Schematic diagram of the working principle of STM [Debata et al., 2018] and (b) photograph of a commercial Omicron LT STM

vacuum (10^{-10} – 10^{-11} mbar). The ultrahigh vacuum prevents the sample surface from oxidation and maintains the tunneling process smoothly. Also, low temperature is preferred to reduce the thermal drift of the atoms. An STM not only produces the image of a sample surface with atomic resolution but also gives information on the density states of occupied and unoccupied states through scanning tunneling spectroscopy (STS). To obtain STS spectra, the tip is placed on a desired point on the surface and a tunneling current with different bias voltages (I-V curve) are recorded. The differential tunneling conductance (dI/dV) is acquired with the help of a lock-in

amplifier. The plot of dI/dV as a function of bias voltage gives the density of states of the occupied and empty states. The HOMO-LUMO energy gap of the sample is determined by the energy gap between the occupied and empty states. The photograph of a commercial ultra-high vacuum low-temperature STM instrument is shown in Figure 2.11b.

2.2.8 Absorption Spectroscopy

Absorption spectroscopy is a useful tool to measure the amount of absorption of electromagnetic radiation by a material. When electromagnetic radiation interacts with the material, some part of the radiation is absorbed by the material. The amount of the absorption depends on the wavelength of the electromagnetic radiation. The infrared (IR) and ultraviolet-visible (UV-VIS) spectroscopy are the most commonly used absorption spectroscopy. Absorption spectroscopy is widely used in molecular and atomic physics. When electromagnetic radiation interacts with molecules or atoms, several things can happen. If the rotational states of the molecules or atoms change upon electromagnetic irradiation, the spectral lines lie in the microwave spectral region. If the vibrational state of the molecules or atoms changes upon irradiation, the absorption spectra lie in the IR region. If the electronic state of the molecules or atoms changes, then the absorption spectra lie in the UV-VIS region. In this work, only UV-VIS spectroscopy is used. In UV-VIS spectroscopy, the absorption is in the UV-VIS range. When a photon is absorbed by a molecule, the molecule becomes excited. If the photon has an energy greater than or equal to the gap between HOMO and LUMO orbitals, it can promote the electrons from HOMO to LUMO. The HOMO and LUMO orbitals are known as bonding and antibonding states and the gap between them is the band gap of the material. The UV-VIS spectra arise because of the electronic transition from bonding to anti-bonding orbitals. The most common transitions that lie in the UV-VIS region are $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, where π orbital arises due to the double bond and n orbitals are nonbonding orbitals. π^* is the antibonding π orbital.

The absorbance can be defined as $A = \log\left(\frac{I_{L0}}{I_L}\right) = \log\left(\frac{1}{T_m}\right)$ where I_{L0} and I_L are the intensity of light before passing through the sample and after passing through the sample, respectively, and T_m is the transmittance. According to Beer-Lambert's law, the absorbance follows the expression: $A = \varepsilon_m Lc$ where ε_m is the molar absorptivity, L is the path length, and c is the concentration of the sample. Using Beer-Lambert's law concentration of an unknown sample can be determined. The basic structure of a UV-VIS spectrometer is shown in Figure 2.12a. Light from a light source is passed through a monochromator and then incident on the reference and the sample with the help of a halfway mirror. The monochromatic light then is passed through the reference and sample and collected using a detector. The absorbance of the sample is recorded as a function of light wavelength. The photographs of a commercial UV-VIS spectrometer are shown in Figure 2.12b-c.

2.2.9 Fluorescence Spectroscopy

Fluorescence is a process of emission of light by a material when electromagnetic radiation having energy greater than the band gap is absorbed by the material. When electromagnetic radiation in terms of a photon with sufficient energy is incident on a molecule or nanostructure, electrons can have excited from the ground state or lower energy state to the excited state. Then the electron relaxes from the higher excited state to the LUMO state by losing its vibrational energy with a non-radiative transition. Immediately the electron jumps from the LUMO state to the ground state and loses its energy by emitting a photon. As a photon is generated in the transition from LUMO to a lower energy state, there will be an emission of light. This phenomenon is known as fluorescence. Generally, the energy of the photon emitted is less than the energy of the photon absorbed in fluorescence. Therefore, the material emits a longer wavelength than it absorbs in fluorescence. This process is very fast (a few ns). There is another term called photoluminescence which is similar to fluorescence, but in photoluminescence, the energy of the emitted photons is equal to or less than the absorbed photons. Fluorescence spectroscopy is a useful nondestructive tool to analyze the fluorescence from the sample. In a

fluorescence spectrometer, light from a light source is passed through an excitation monochromator and then the monochromatic light is passed through the sample. Then the light will be emitted from the sample because of the fluorescence process. The emitted light or electromagnetic radiation is then passed through another monochromator called an emission monochromator and then collected in a detector. The schematic diagram of a fluorescence spectrometer is shown in Figure 2.13a. The fluorescence spectrometer can generate emission spectra and excitation spectra. The quantum yield of fluorescence can be determined as

$$Q.Y. = \frac{number\ of\ photons\ emitted}{number\ of\ photons\ absorbed}$$

Quantum yield can have a maximum value, ideally 1.0, but in reality, it has a value less than 1. The materials having a fluorescence quantum yield greater than 0.10 are considered quite good. The photograph of a fluorescence spectrometer is shown in Figure 2.13b.

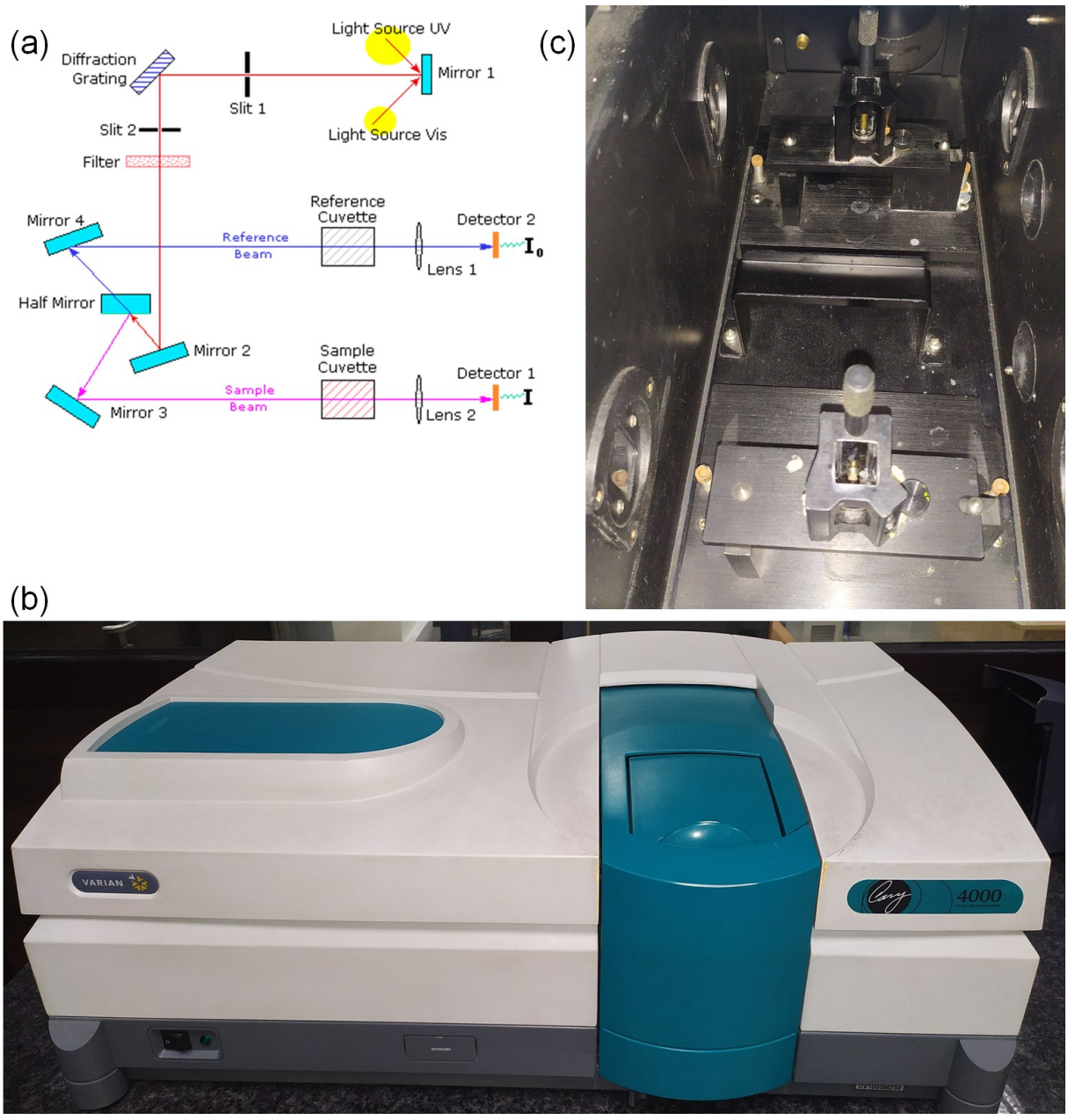

Figure 2.12: (a) Schematic diagram of absorption spectrometer and (b) – (c) photographs of a commercial UV-VIS spectrometer

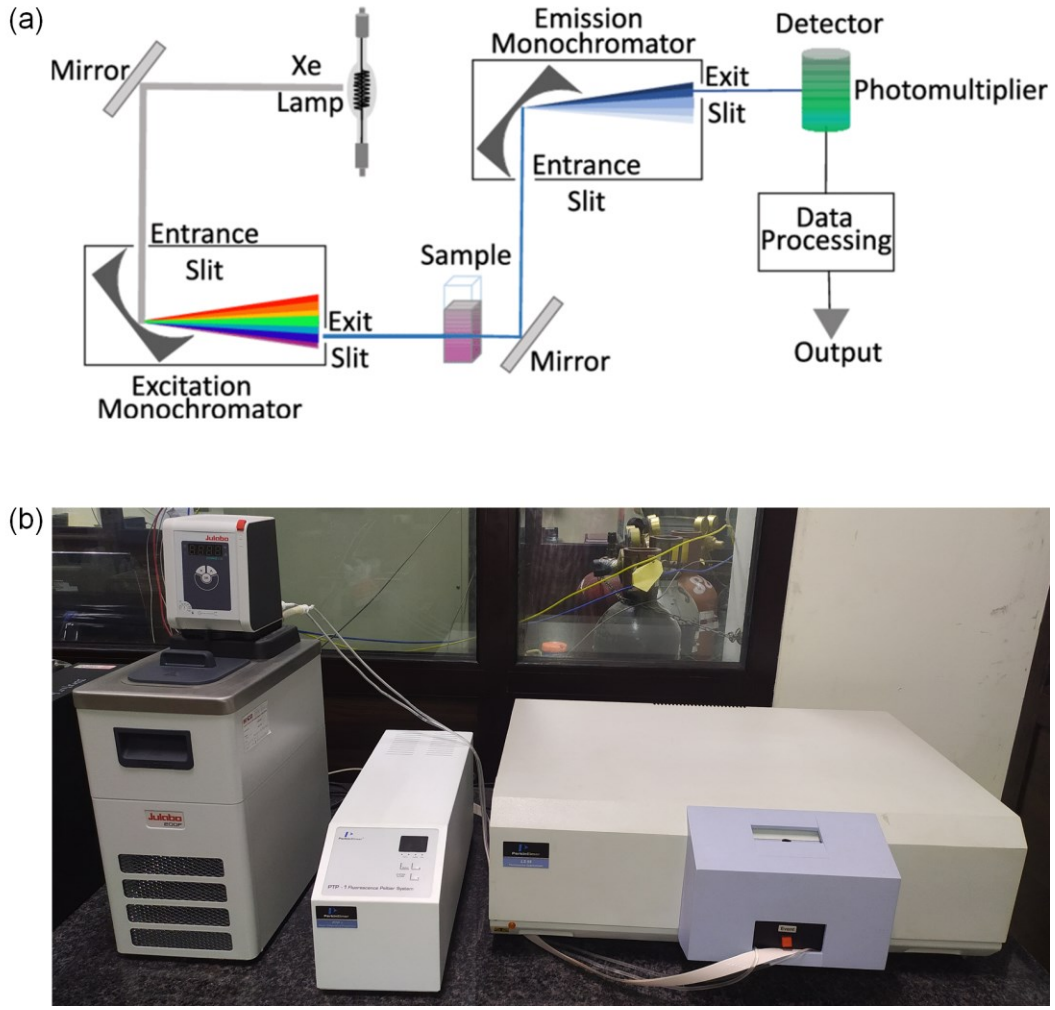

Figure 2.13: (a) Schematic diagram of the working principle of fluorescence spectrometer and (b) photograph of a commercial fluorescence spectrometer

2.2.10 Device Characterization Setup

For the electrical characterization of the device, a homemade probe station with two probe configurations has been used in this work as shown in Figure 2.14a. The probes are adjusted on the electrodes of the device with the help of two spring-loaded micro positioners as shown in Figure 2.14b. The I-V characteristics of the device have been measured using a Keithley 6430 sub-femtoamp sourcemeter. For the programming of the I-V, retention and "read-write-erase" measurements, the LabVIEW program has been used. For temperature dependent I-V, a sample stage heater with controller has been used as shown in Figure 2.14c-d.



Figure 2.14: Photograph of the (a) electrical characterization setup and (b) two probe system with micro positioner (c) substrate heater controller unit and (d) sample stage heater setup