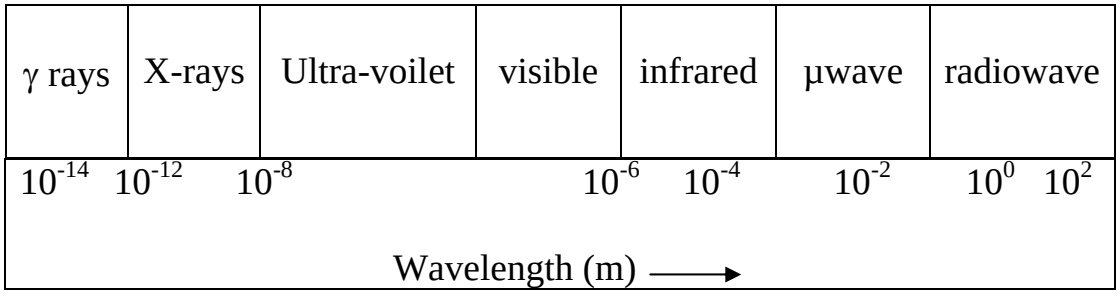
2.1 Characterization Techniques:

The metal nanostructures are extensively characterized by several characterization techniques e.g. UV-visible spectroscopy, Fourier transform infrared spectroscopy (FT–IR), Transmission Electron Microscopy (TEM), Scanning Electron Microscope (SEM), X-ray Photoelectron Spectroscopy (XPS), cyclic voltammetry (CV) & amperometry and further its electrochemical applications are anticipated by voltammetric/amperometric techniques. The working principle, important formulae and instrumentation have been discussed in the following segment.

2.1.1 UV Visible spectroscopy:

Spectroscopy deals with study of interaction of electromagnetic wave with matter. The interaction of atom/molecule with electromagnetic wave result into the some change occurs within the atom/molecule can be rationalized as follows:

- X-ray: core electron excitation
- UV visible: valance electronic excitation (bonding electrons),
- IR: molecular vibrations
- Radio waves: Nuclear spin states (in a magnetic field)



There are two type of light illuminating source used in UV visible spectroscopy. First one is hydrogen-deuterium lamps as they cover the whole UV region (200-400 nm) and other is tungsten filament lamps, as specifically it emit the radiations above to 375 nm (375-2500 nm), hence used in visible region. UV visible spectroscopy is an important tool to locate the absorption band in materials science. The other name of UV (Ultra-Violet) spectroscopy is electronic

spectroscopy, as it involves the promotion of the electrons from the ground state to the higher energy or excited state within the molecule having particular electronic environment is schematics below in figure 2.1.

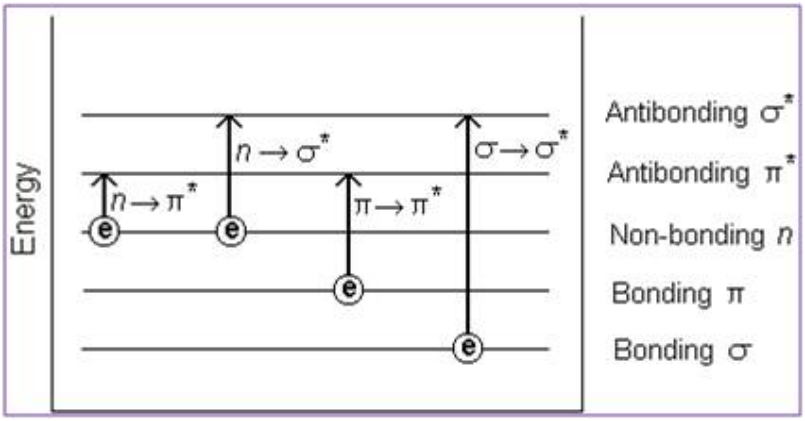


Figure 2.1: Electronic transition in a molecule.

Generally, in the recent terminology, the most favored transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). UV spectroscopy obeys the Beer-Lambert law which states that, when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as concentration of the solution. Basic instrumentation for UV visible spectroscopy is represented as figure 2.2.

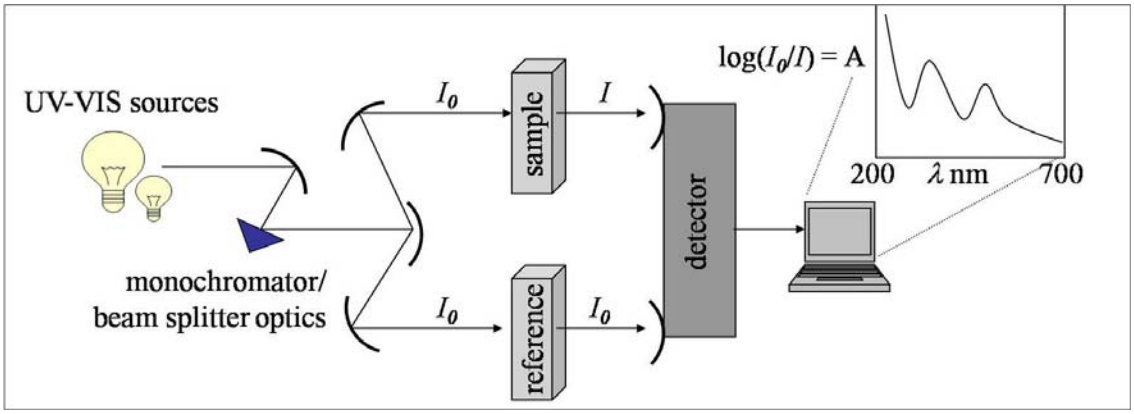


Figure 2.2: Block diagram of UV visible spectroscopy.

Beer-Lambert law states that linear relationship between absorbance and concentration of an absorbing sample under constant conditions of the path length and the incident wavelength of the light. The schematic illustration of Beer-Lambert law is given in Figure 2.3.

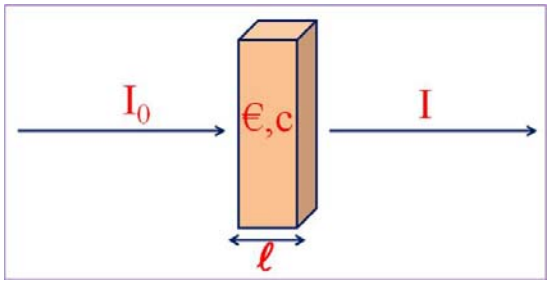


Figure 2.3: Schematic ray diagram illustrating Beer-Lambert law.

$A = \log (I_0/I) = €cl$

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy.

Where, A = absorbance

I_0 = intensity of light incident upon sample cell

I = intensity of light leaving sample cell

c = molar concentration of solute

l = length of sample cell

€= molar absorptivity

Specific UV visible absorption band for noble metal (Ag, Au) known as surface plasmon band which is not present in their bulk metal counterpart or its respective ions. Origin of surface plasmon resonance is due to coherent interaction of the electrons in the conduction band with electromagnetic radiation. UV-vis spectroscopy is a broadly used tool for the characterization of noble metal nanoparticles as the optical properties of nanoparticles are sensitive to the size, shape, concentration of the nanoparticles as well as the dielectric environment [Skoog *et al.*, 2010; Harvey *et al.*, 1956]. As a part of research work we have

exclusively utilized UV visible technique to locate the absorption spectrum of metal nanostructures in this thesis.

2.1.2 Fourier transform infrared spectroscopy (FT–IR):

Functional groups attached to the metal nanoparticle surface show different FT–IR pattern than those of free groups, hence FT–IR provide information about the surface chemistry of nanomaterials. Identification of specific types of chemical bonds or functional groups based on their unique absorption signatures is possible by infrared spectroscopy.

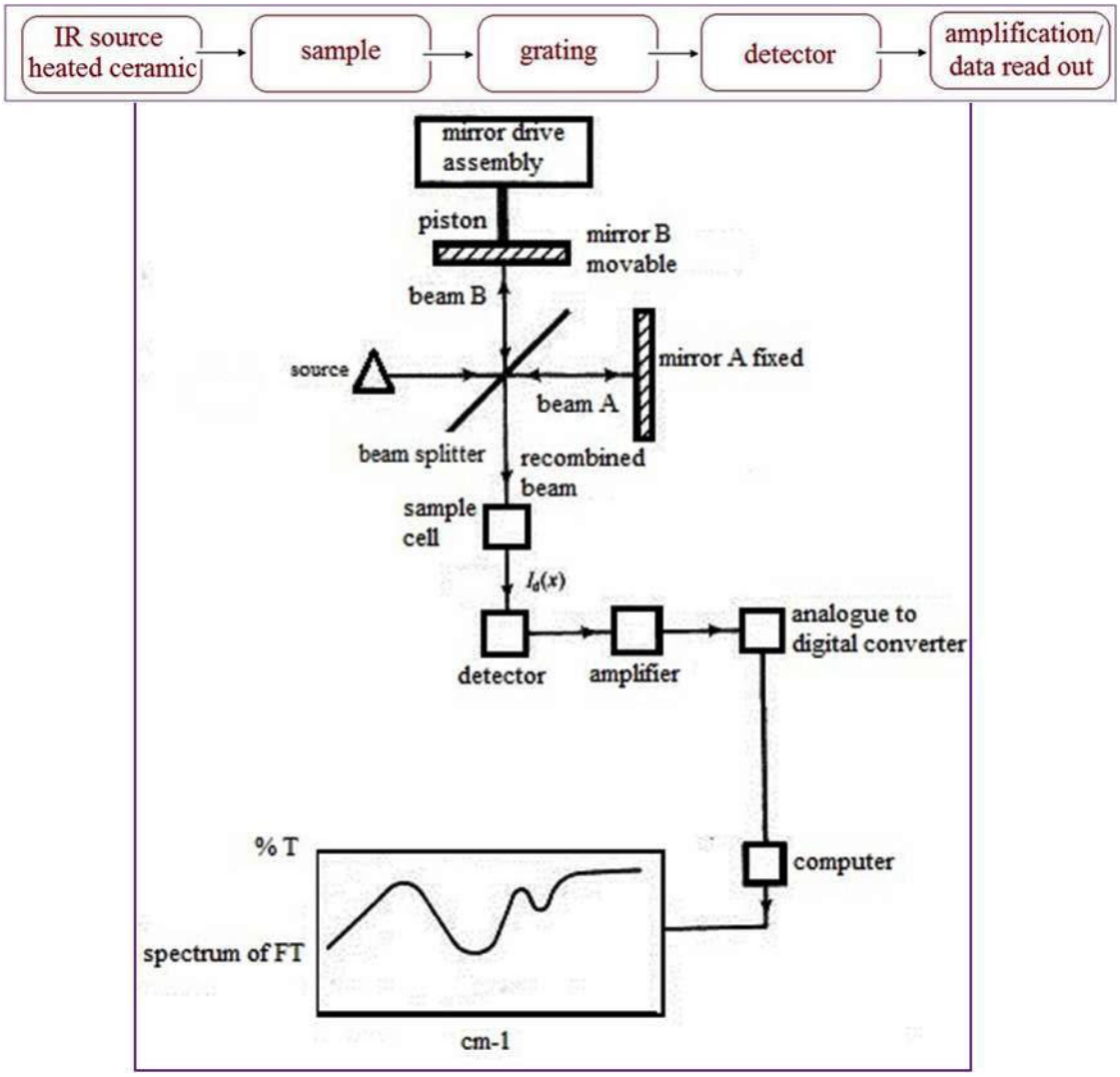


Figure 2.4: Block diagram for FT–IR.

Infrared radiation does not have enough energy to induce electronic transitions as UV-visible, hence bond stretching and bending is possible by absorption of energy. Absorption of Infrared radiation is restricted to compounds with small energy differences in the possible vibrational and rotational states. For a molecule to absorb Infrared radiation, vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration. The most useful Infrared radiation region for the spectrum interpretation lies between 400–680 cm^{-1}.

When a molecule absorbs infrared radiation, one of its bonds experiences a change in characteristics vibrational energy which reflects in the typical IR spectrum. Each bond has a characteristic frequency (in the infrared part of the electromagnetic spectrum). Infrared spectrometers employing an *interferometer* and having no monochromator is used now a days. These non-dispersive instruments, known as Fourier transform (FT) spectrometers, have increased sensitivity and can document spectra much more rapidly than the dispersive type [Skoog *et al.*, 2010; Harvey *et al.*, 1956]. Particular frequency which matches the characteristic frequency of a specific bond will be absorbed, get reflected in a spectrum. Typical block diagram for FT–IR instrumentation as shown in figure 2.4.

We have utilized FT–IR technique as preliminary studies to interpret the interaction (S–Au, N–Au, S–Ag, N–Ag). Nano gold/ silver interacts with nitrogen or sulphur atom present in the molecule, thereby electron density get transferred from organic functionalities to metal surface hence the characteristics vibrational stretching (C–H, N–H, S–H, C–N, C–S) frequency get changed as interpreted (case a vs. case b) in figure 2.5.

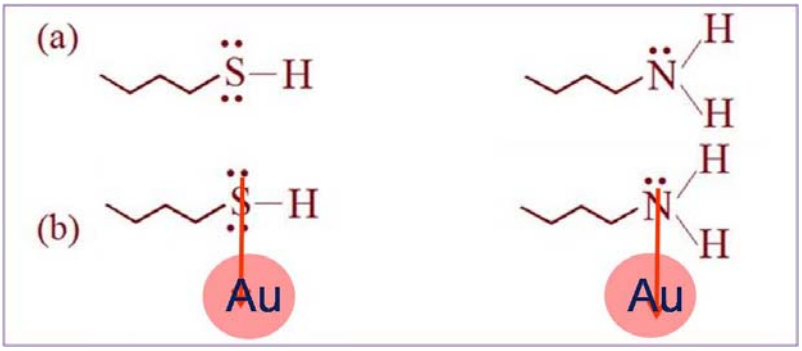


Figure 2.5: Scheme illustrating the transfer of electron density from non-metal to metal atom, resulting into the change in the characteristics vibrational frequency.

FT–IR plot is (%) transmittance Vs vibrational frequency in wavenumbers (cm^{-1}). The FT–IR measurements of film and powder samples were conducted in transmission mode.

2.1.3 X-ray Photoelectron Spectroscopy (XPS):

Irradiation of a sample surface with monochromatic X rays is called X-ray photo electron spectroscopy. It is also termed as electron spectroscopy for chemical analysis (ESCA). Figure 2.6 illustrating the schematics the representation of the physical process concerned in XPS. X-ray photoelectron spectroscopy based on the photoelectric effect. The three lower lines labeled as E_b $E`_b$ $E``_b$ represent the energy of the inner shell K and L electron of an atom. The upper lines are the energy level of the outer shell/ valance electron. One of photon of the monochromatic X rays beam of known energy hυ displaces an electron from K orbital of an energy $E_{b.}$ and the process can be represented as

$$A + h\upsilon \longrightarrow A^{*+} + e$$

A can be atom, molecule or an ion and A^{*+} is the corresponding excited state. The kinetic energy of an emitted electron E_K is measured with an electron spectrometer, hence binding energy of the electron E_b can be measured by the following equation where, W is work function of the spectrometer.

$$E_b = h\upsilon - E_K - W$$

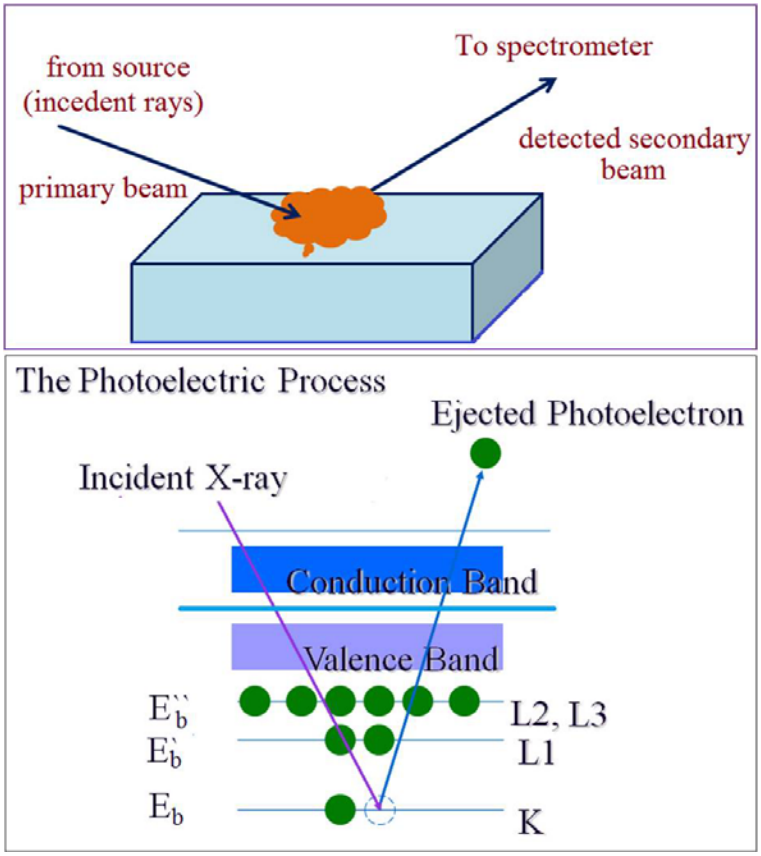


Figure 2.6: Physical process involved in XPS.

Common way of spectroscopic surface measurement comprise the irradiation of sample with a primary beam made up of photon, electrons and impact of this on the surface result in the formation of secondary beam from the substrate which is measured/detected by the spectrometer as shown in figure 2.7 (schematic diagram for instrumentation). XPS spectrum is the plot of intensity (count/sec) vs. binding energy (eV). Wide scan XPS spectrum called survey spectrum which generally scan from 0 to 1200 eV binding energy. In the present thesis we have utilized XPS spectrum for elemental analysis and identification of oxidation state of the synthesized nanomaterials [Skoog *et al.*, 2010; Harvey *et al.*, 1956].

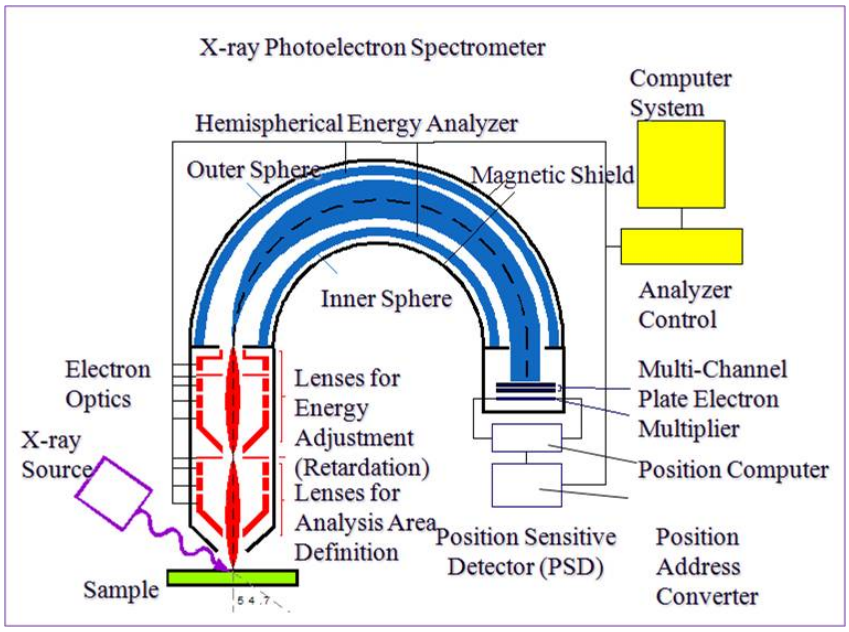


Figure 2.7: Block diagram of modern electron spectroscopy for chemical analysis.

2.1.4 Scanning Electron Microscope (SEM):

The SEM is a type of electron microscope capable of producing high resolution images of sample surfaces. For obtaining SEM image a finely focused beam of electron incident on the surfaces of the specimens. The beam of electron is scanned across the sample in a raster fashion by raster coils. The resulting scanning pattern is similar to that used in cathode ray tube (CRT) of a television set in which the electron beam is (1) swept across the surface linearly in the X direction, (2) returning to its starting position, (3) shifting downwards in the Y direction by a standard increment. This process is repeated until a desired area of the surface has been scanned. In a digital system signal is received from the Z direction and stored in a computer, ultimately converted to an image. In SEM instrument back scattered and secondary electron are used to construct an image [Skoog *et al.*, 2010; Harvey *et al.*, 1956].

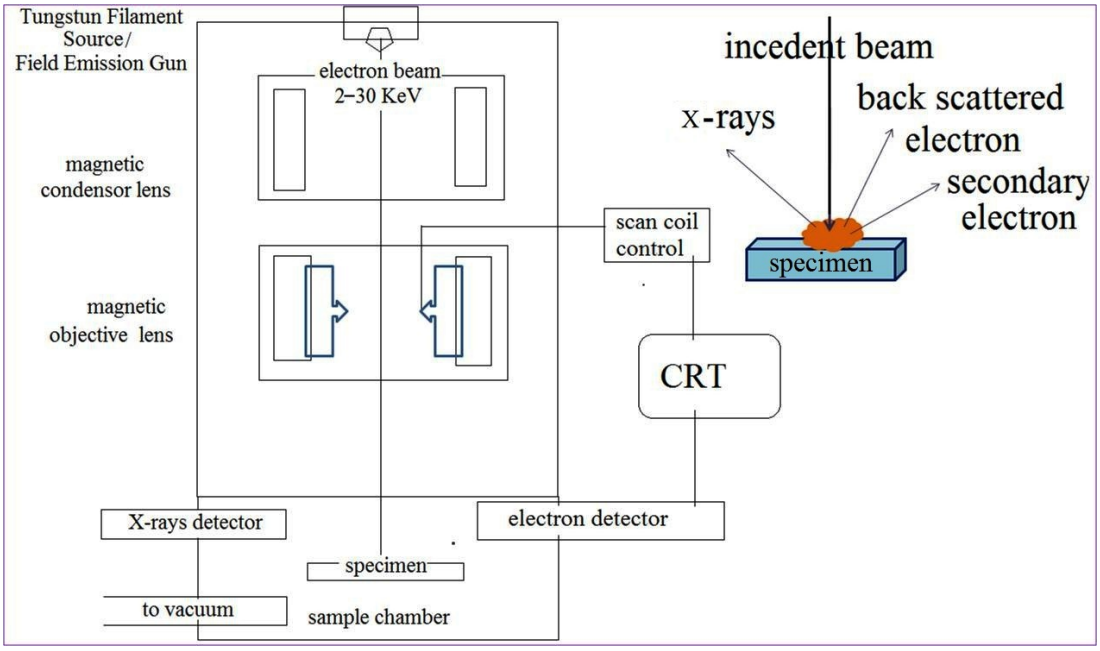


Figure 2.8: Block diagram of scanning electron microscopy for surface analysis.

For chemical analysis purposes modern SEM utilizes the X-ray detectors that allow qualitative and quantitative determination of the sample by means of X-ray (EDAX) as illustrated in figure 2.8. Measuring energy of emitted characteristic X-rays allows the identification of element composing the area of sample analyzed.

2.1.5 Transmission Electron Microscopy (TEM):

TEM is a electron microscopy technique in which high resolution images of the thin samples (colloidal solution casted on grid) is achieved by using a beam of high energetic electrons. It provides an approach to characterizing morphology, dimensions and distribution of the nanomaterials in the sample. The emission source which is otherwise known as the electron gun emits the electrons that travel down a column and which is focused by the condenser lens into a very thin beam. The beam of electrons illuminates the specimen on the specimen holder. Depending on the density of the material present, some of the electrons are scattered and disappear from the beam as shown in figure 2.9. The transmitted electrons are focused into an image by the objective lens, followed by traveling through the projective lens to magnify the image.

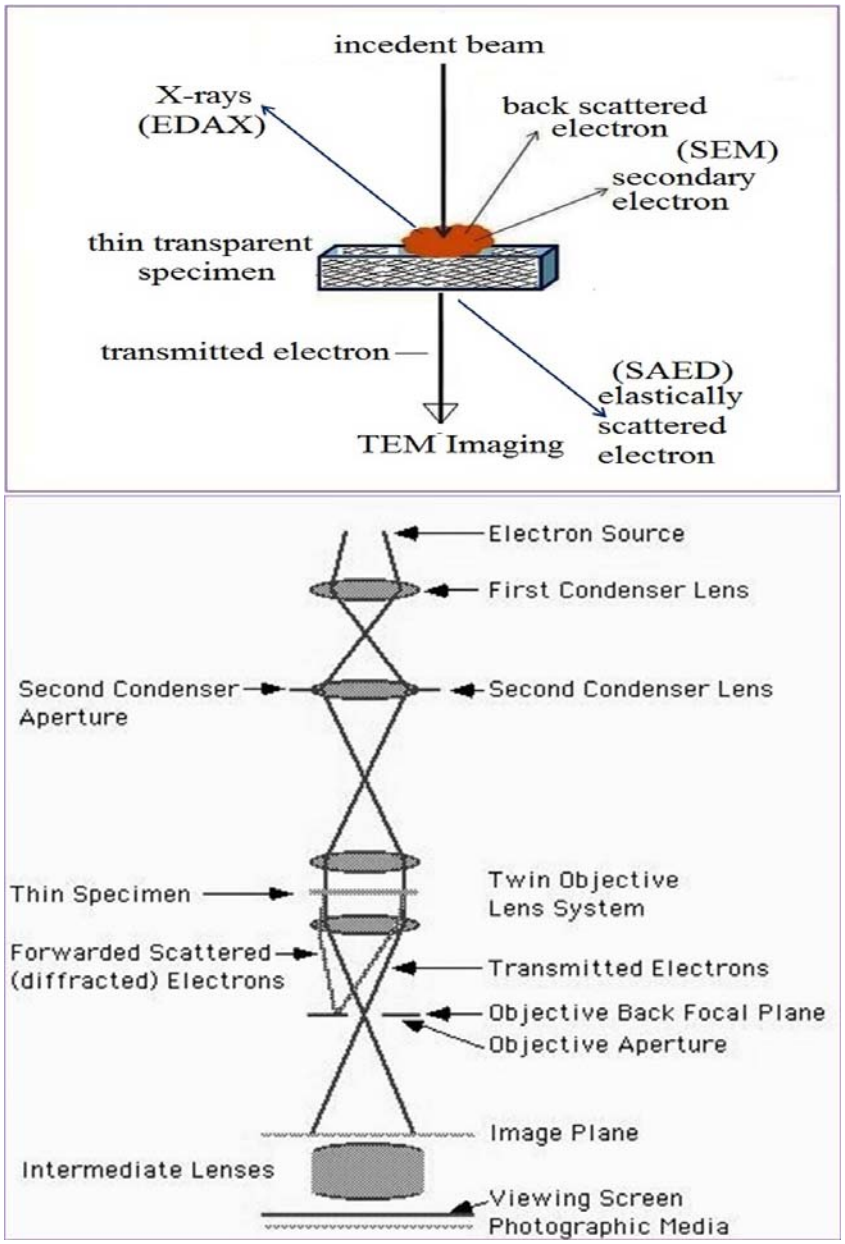


Figure 2.9: Block diagram of transmission electron microscopy for surface imaging.

The electron intensity distribution behind the specimen is magnified with a three or four stage lens system and viewed on a fluorescent screen as shown in figure 2.9. The image can be recorded by direct exposure of a photographic emulsion or an image plate or digitally by a CCD camera. In a typical TEM a static beam of electrons at 100 – 400 KeV accelerating voltage passes through in a region of an

electron transparent specimen which is immersed in the objective lens of the microscope [Williams *et al.*, 2010; Skoog *et al.*, 2010].

2.1.5.1 Bright Field (BF) and Dark Field (DF) imaging:

In BF imaging, only the transmitted beams are allowed to pass objective aperture to form images while in DF imaging, only diffracted beams are allowed to pass the aperture to form the images.

2.1.5.2 Basic features of electron diffraction:

The separation of the diffraction spot on the diffraction pattern can be directly used to determine interplanar spacing (d) in the nanocrystals. To do so, we need to use camera equation which is simply derived by taking the consideration of Bragg's law. The transmitted and diffracted electrons are recombined by the objective lens to form a diffraction pattern in the back focal plane of that lens.

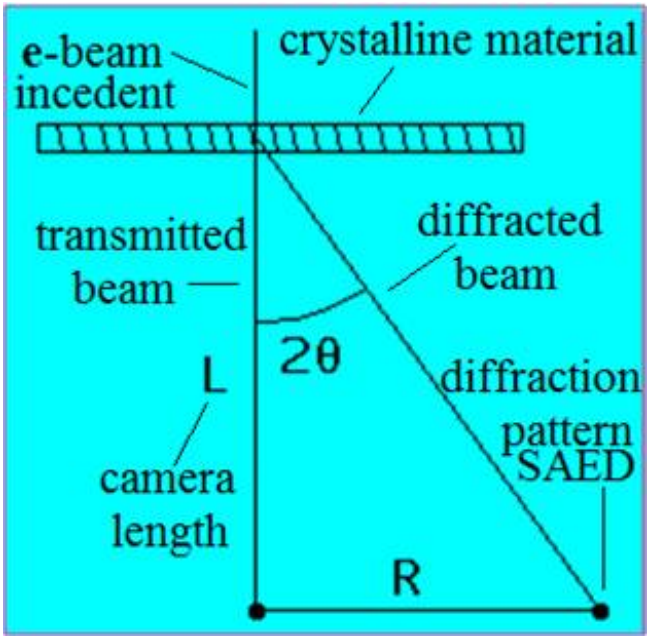


Figure 2.10: Ray diagram of SAED, illustrating electron diffraction.

From the figure 2.10

$\lambda = 2d\sin\theta = 2d\theta$ (if, $\sin\theta \cong \theta$)

$R/L = \sin 2\theta = 2\theta$

$\lambda = d\,(R/L)$

L λ= d R

L is "camera length"

$$\mathbf{L\,\lambda = d\,R}$$

L λ is "camera constant"

1/d is the reciprocal of interplanar distance ($Å^{-1}$). A reciprocal lattice is another way of view a crystal lattice and is used to understand diffraction patterns. A dimension of 1/d is used in reciprocal lattices [Williams *et al.*, 2010; Skoog *et al.*, 2010]. By using this relation one can index the SAED pattern of crystalline nanomaterials (hkl) values.

2.1.5.3 Phase Contrast/ Lattice Imaging/ High Resolution Transmission Electron Microscopy (HRTEM):

By using all of the diffracted and non-diffracted (transmitted) beams (by using a large objective aperture) and add them back together phase and intensity, to form a phase contrast image. HRTEM is the way in which lattice fringes of the nanomaterials can be seen which is the characteristics of the nanomaterials.

2.1.6 Electrochemical voltammetric techniques, associated terminology and its working principle:

In the following section, basic components of electrochemical instrumentation and working principles have been presented. Electroanalytical method that depends upon the measurement of the current as a function of applied potentials is called *voltammetric* method.

2.1.6.1 Cyclic voltammetry and amperometric technique:

In voltammetry, voltage of working electrode is varied systematically while the current response is measured and several different voltage time functions called *excitation signal* in voltammetry as illustrated in figure 2.11. The very simplest is the linear scan in which potential of the working electrode linearly varied with time typically ranging from –2.2 to +2.2 volts with references to particular reference electrode depending upon the aqueous and non aqueous electrochemistry. Figure 2.11 (a) illustrating the scanning potential w.r.t. time and at the same time

measuring corresponding current is called *linear scan voltammetry* and once again scanning back the potential to its original position is called *cyclic voltammetry* figure 2.11 (b). Cyclic voltammetry is the most important techniques for the study of electrochemical redox reaction/electron transfer studies.

Another voltammetric technique is so called *amperometry* in which, constant potential is applied to the working electrode and current is measured as a function of time. Since the potential is not scanned, amperometry does not lead to a voltammogram. It is most often technique used in the construction of electrochemical sensors that is used for the qualitative/quantitative analysis of analytes.

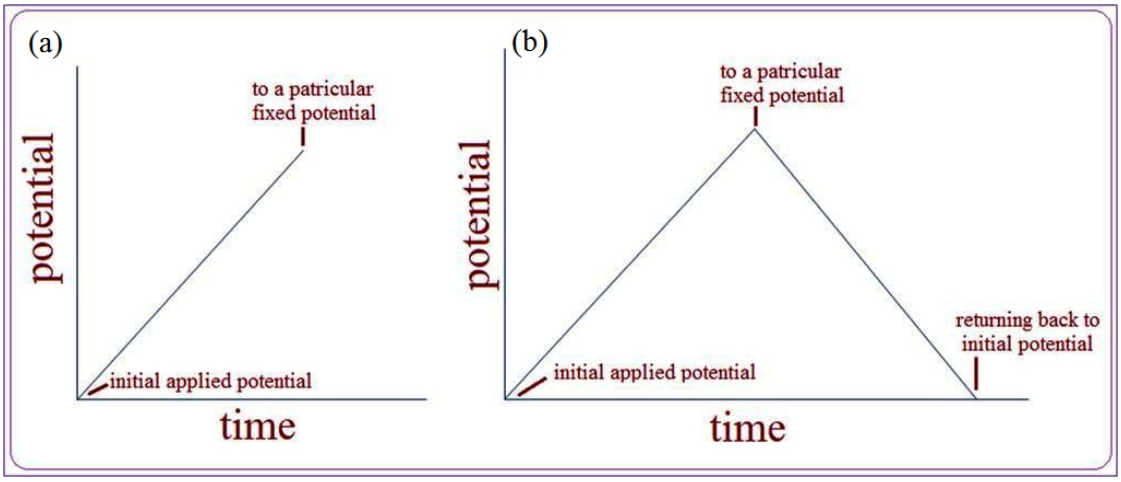


Figure 2.11: Common excitation signal in voltammetry.

The peak current in a cyclic voltammogram containing only one species is described by Randles Sevick equation:

$$i_p = (2.69\times10^5)\, n^{3/2} AD^{1/2} v^{1/2} C^*$$

Where i_p is the peak current, n is the number of electrons transferred, A is the electrode area, D is the diffusion coefficient of the species, v is the scan rate and C^* is the bulk concentration of the species at 25 °C. *Galvanostat* is used for dynamic methods, in which it is necessary to control the current flowing through an electrochemical cell and *Potentiostat* is used to control the potential flowing through an electrochemical cell. Electrochemical measurements are made in an

electrochemical cell, consisting of three electrodes and associated electronics for controlling & measuring the current/ potential. Specific experimental electrochemical set up design in detail as shown in figure 2.12. The potential of one of the electrodes is sensitive to analyte's concentration & upon which electrochemical redox reaction take place so called *working* or *indicator electrode***.**

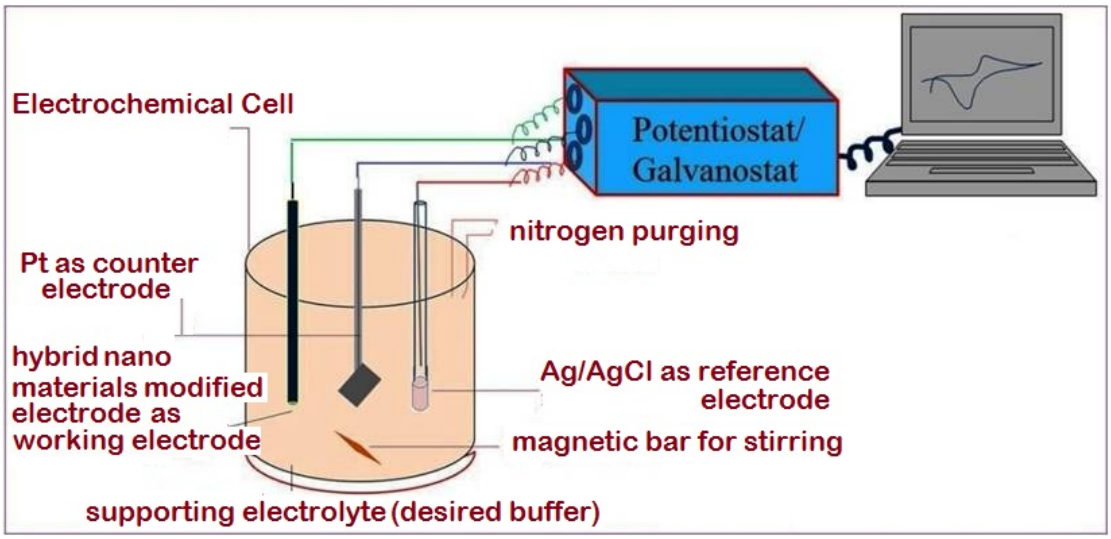


Figure 2.12: Electrochemical set up for voltammetric measurement.

The second electrode, which is called the *counter electrode*, serves to complete the electric circuit. The third electrode, which is called the *reference electrode* whose potential is known w.r.t. standard hydrogen electrode (0.00 V) and measure the potential of working electrode w.r.t. reference electrode & which is irrespective of analyte concentration [Bockris *et al.*, 2000; Skoog *et al.*, 2010].

2.1.6.2 Faradaic & nonfaradaic current and it's consequences:

Analytes reduces or oxidizes at the vicinity of the electrode surface depending upon the particular electrode reaction thereby generates the electron and produce the electric signal. Current produced due the electrochemical redox reaction occurring at the electrode/ electrolytes surface is called faradaic current. Other currents may also exist in an electrochemical cell that is not related to redox

reaction is called *non faradaic currents* and must be minimized for voltammetric measurement.

Concentration polarization occurs because of the finite rate of mass transfer from solution (electrolytes) to the electrode surface. There are three modes of mass transport that influence the rate at which reactants and products are transported to and from the electrode surface: *diffusion*, *migration* and *convection*.

Diffusion is the movement of a species under the influence of concentration gradient ions/ molecules move from a region of higher concentration region to lower concentration region. *Convection* is the transport of ions/ molecules through a solution as a result of stirring/ vibration/ temperature gradient. The electrostatic process in which ions move under the influence of electric field is called *migration*. Migration of analytes is the undesired things in the voltammetry. Migration can be eliminated by adding a high concentration of an inert electrolyte to the analytical solution is called *supporting electrolyte*. Supporting electrolyte also reduces the IR (resistance) drop of electrochemical cell. The most important example of a non faradic current occurs whenever the electrode's potential is changed. The negatively charged particles in solution migrate toward a positively charged electrode and positively charged particles move away from the same electrode. The movement of charged particles in solution gives rise to a short-lived, *charging current (capacitive current)* which is *non faradic* in nature. Even in the absence of analytes, a small current flows through an electrochemical cell, this current is called the residual current also *non faradic* in nature, which is due to the reduction of dissolved oxygen or may be due to trace unwanted foreign substances in the supporting electrolyte, this is why nitrogen gas is generally purged before voltammetric experiment to avoid reduction/oxidation peak which interfere the detection of desired analytes [Bockris *et al.*, 2001; Skoog *et al.*, 2010].