Chapter 2

Methodology

In this chapter at first we briefly describe the synthetic procedures adapted to synthesize basic nanoparticles and membranes that have been employed in this thesis. Different experimental techniques employed to characterize the nanoparticles, residues obtained in course of water treatment and prepared membranes, have also been described later in this chapter.

2.1 Synthesis

2.1.1 Nanoparticle

We have used colloidal method of hot injection based protocol under inert atmosphere for the synthesis of nanocrystals. This method includes mainly a reaction medium of high boiling organic solvents, cationic and anionic precursor and organic surfactants with long hydrophobic chains to stabilize the nanocrystals. We have used single as well as multi source precursor in hot injection based method. Following this procedure, we have synthesized the ZnS nanorods. It is generally a two step process, firstly the precursor is produced and then from the precursor
ZnS nanorods are produced [1].

**For Zinc ethyl xanthate preparation:** At first, in 250 ml of water, 3.00 g of potassium ethyl xanthogenate was dissolved. Separately in another beaker 3.48 g of zinc perchlorate hexahydrate was dissolved in 100 ml of water. The metal salt solution was added into the xanthate solution in small amounts and zinc xanthate salt precipitated out. The salt was washed 5 times with water, filtered and dried in air.

**For ZnS rod preparation:** The reaction was carried out in a glass test tube immersed in hot silicone oil where, 1.53 g of Octadecylamine (ODA) was purged with CO$_2$ and the temperature was increased to 100 °C. Molten ODA was treated continuously with CO$_2$ for around 10-15 mins to convert it to octadecylammonium octadecylcarbamate (ODOC). Next the purging gas was changed to argon. To the molten ODOC, 0.08 g of zinc-ethylxanthate (precursor) was added after 10 minutes of argon purging. The color changed to yellow 2-3 mins after addition of precursor, then the temperature was raised to 105 °C where, white turbidity was observed. It was kept in 105 °C for around 5 mins and again the temperature was increased to 130 °C where, it was annealed at 130 °C for 10 mins. The reaction was stopped and left to cool down to room temperature, after that Ar-supply was switched off. After cooling, the sample was flocculated by adding methanol and finally separated by centrifugation, redispersing in chloroform and dried in air.

![Figure 2.1](image.jpg)

**Figure 2.1:** TEM images of (a) as synthesized ZnS nanorods and (b) residue obtained from treating ZnS nanorods with As-contaminated synthetic water.
These as prepared ZnS nanorods were used to treat arsenite contaminated ground or synthetic water in presence of Fe(III) and were also tested against other common contaminants like iron (II) or (III) and lead (II) separately. Around 1 mg of ZnS nanorods were used for lab scale treatment. The treatment of contaminated water was carried out for 3 hours at 70 °C under constant stirring. It was then cooled down at room temperature and was filtered with Whatman 42 filter paper. The formed residue and filtrate were collected for further analysis.

2.1.2 Membranes

Membranes were synthesized using drop cast technique [2], where membrane-starting material was dissolved in solvent and the formed solution was cast in a flat surface and allowed to dry, followed by annealing in a non-solvent like water. Cellulose acetate (CA) was used as the mother material which was cross linked separately with glutaraldehyde and malic acid (25% w/w solution in water). This mixture of CA and crosslinker was dissolved in acetone to form 4% w/w solution w.r.t initial CA. The solution was drop cast in a flat S-line petri dish and left to evaporate overnight. Finally the membranes were annealed in milliQ water at 80 °C (see Figure 2.2). The formed cross linked membrane was tested for FO flux, salt rejection and its cross linking effect on overall tangential membrane strength.
2.2 Characterization Tools

2.2.1 Inductively Coupled Plasma - Optical Emission Spectroscopy / Mass Spectroscopy (ICP-OES/MS)

Inductively coupled plasma-optical emission spectroscopy is used to detect and quantify the elements of a sample specimen. It is an analytical technique used for the detection of trace metals. ICP-MS and ICP-OES are designed to determine the composition of a wide variety of materials and has an excellent sensitivity. It generally consists of two parts (i) The excitation source Inductively Coupled Plasma (ICP) and (ii) the detector which may be Optical Emission Spectrometer (OES) or Mass Spectrometer (MS) [3].

Inductively Coupled Plasma (ICP)

Inductively Coupled Plasma (ICP) is the excitation source used in Optical Emission Spectroscopy (OES) and Mass Spectrometry (MS) instruments. The ICP source consists of a quartz torch inside a radio frequency (RF) coil generally made of Copper. The plasma torch consists of three concentric quartz tubes namely the inner, the intermediate, and the outer tube. The nebulizer gas flow which helps to create a fine aerosol of the sample solution is carried through the inner tube of the torch and into the plasma. The intermediate tube carries the auxiliary gas. The auxiliary gas flow helps to lift the plasma off of the inner and intermediate tubes to prevent melting and the deposition of carbon and salts on the inner tube. The outer tube carries the plasma gas, which is used to form and sustain the plasma. The tangential flow of the plasma gas through the torch constricts the plasma and prevents the ICP from expanding to fill the outer tube, preventing
the torch from melting. Argon gas is generally the plasma gas, which is passed through the torch and RF energy is applied to the coil. When a spark is added to the highly energized argon atoms, electrons are stripped from argon, and the plasma is ignited. The argon ions and free electrons are further agitated by the RF field, causing the temperatures within plasma torch to reach approximately 6000 - 10,000 K (see Figure 2.3).

![Figure 2.3: Inductively Coupled Plasma (ICP) torch.](image)

Generally samples in ICP measurements is introduced in liquid form, therefore solid materials is needed to be dissolved in an aqueous/organic solution prior
to analysis (though laser ablation is used for non-dissolving samples. A peristaltic pump delivers an aqueous or organic sample into an analytical nebulizer. The liquid is converted to an aerosol using the nebulizer (argon is generally used as the nebulizer gas) and is then sprayed into the center of the plasma through the inner tube. A wide variety of nebulizer types are available, including pneumatic (concentric and cross-flow), grid, and ultrasonic nebulizers. Micronebulizers, high efficiency nebulizers, direct injection high-efficiency nebulizers, and flow-injection nebulizers are also available. The selection of the nebulizer for a given analysis depends on the sample matrix, analyte, and sensitivity desired. After nebulizer the sample enters the spray chamber, which is designed to permit only the smallest droplets of sample into the plasma. The spray chamber functions to remove the larger sample droplets generated during the nebulization process. Typically only 1% to 2% of the sample aerosol reaches the ICP. There are more than one type of spray chamber available for use with ICP, like the Scott double-pass spray chamber, as well as cyclonic spray chambers of various configurations. The spray chamber has to be compatible with the sample and solvent and must equilibrate and washout in as short a time as possible. Like nebulizer, here also, the nature of the sample matrix, the desired sensitivity, and the analyte should be considered while selecting a spray chamber. After leaving spray chamber instantaneously (in both distance and time), the particles within the aerosol are dried, atomized, ionized, excited and relaxed. It is from this point forward that the two instrument types differ in accordance to the detector employed for analysis.

Optical Emission Spectroscopy (OES)

As discussed the sample immediately breaks into the constitute elements in high temperature of plasma, and the elements are further ionized by the high energy electrons of the plasma. The recombination process of the excited elements
produce the characteristic x-rays for each of the constituent elements of the specimen. It separates the light emitted from the plasma into its discrete component wavelengths using a diffraction grating. Each element in the periodic table has its own distinct set of emission wavelengths. This emitted light are then analyzed by the OES unit to quantify the elemental weight per unit volume.

In today’s equipment, CCD detectors are used to quantify the amount of light at a given wavelength. The amount of light on a given wavelength is proportional to the concentration of the corresponding element in the solution presented for analysis to the instrument within the given calibration range specified for the specific analyte.

**Mass Spectroscopy (MS)**

In Mass Spectrometer (MS) samples, the ions generated in the plasma torch are directed through a quadrupole mass spectrometer. The quadrupole filters the ions based on their mass to charge ratio (m/z) so that only ions with a specific m/z reach the electron multiplier detection system. The signal intensity for a given analyte ion is proportional to its concentration in the solution presented to the instrument, within the specified calibration range. The solution concentration is then used to calculate the mass fraction of the analyte in the material being tested.

The absolute quantification of specified element is done by calibration, consisting of three steps which is similar for both the techniques, (a) analyze blank, (b) analyze standard and (c) analyze sample. The light intensity found in the blank solution corresponds to the element under investigation at zero point of the calibration line. The intensity from the standard reference solution is fixed to the specified amount of the analyte mentioned in reference standard. Finally
the element concentration is calculated using the sample solution by placing the observed intensity in the linear calibration line made from the zero and standard points. Generally, a three point calibration is done taking three different concentration levels of the known reference standard and analyte concentration of unknown samples falls generally within these calibration range. We have used ICP-OES (Perkin-Elmer Optima 2100 DV) and ICP-MS instruments (ICP-MS, Elan DRC-e, Perkin-Elmer) for quantification of different samples.

2.2.2 X-Ray Diffraction (XRD)

Wilhelm Röntgen discovered X-rays in 1895; after seventeen years, Max von Laue realized that the wavelengths of X-rays are comparable to the interplanar distances in a crystal and they might be diffracted when passed through a crystal. Since then, X-ray diffraction (XRD) has emerged out as one of the most important tool to characterize crystalline materials. XRD provides information about the different crystallographic phases present in the system, characterizing the synthesized materials; for nanoparticles, this technique can also provide an estimate of the crystal size as well as interparticle distance. Modern works are very much influenced by the methods developed by William Henry Bragg and his son William Lawrence Bragg. They considered a lattice plane as a mirror and modelled a crystal as stacks of reflecting lattice planes to put forward the Bragg’s law written as:

$$2d \sin \theta = n \lambda$$  \hspace{1cm} (2.1)

where, $d$ is the interplanar distance of lattice planes belonging to the same family, $\theta$ is the glancing angle and $\lambda$ is the wavelength of incident X-ray. Reflections with $n = 2, 3...$ etc. are called 2nd-order, 3rd-order, and so on, respectively. X-rays get scattered by the electrons in the system, thus heavy atoms with a higher electron density gives rise to a stronger scattering comparing to lighter atom; this
dependency on the number of electrons is governed by the structure factor, which ultimately decide the intensity of a diffraction pattern [4, 5].

**Powder X-Ray Diffraction (PXRD):**

It gives a one-dimensional diffraction (1D) profiles, which measured with scanning point detector or linear position-sensitive detectors (PSD). Powder XRD patterns of the nanoparticles and formed residues after water treatment were recorded with a Bruker AXS: D8 Advance powder diffractometer using Cu K$_\alpha$ radiation ($\lambda = 1.54069$ Å) as the monochromatic x-ray source after filtering the K$_\beta$, generated from a x-ray generator. The samples for XRD measurements were prepared by dispersing nanocrystals in suitable solvents (organic or aqueous) and drop casting on a silicon substrate sample holder. Diffraction signal for nanosized crystals are generally weak, thus a slow scan with about 1.5 degree per minute is
required to obtain a good signal to noise ratio. The obtained XRD patterns are compared with the standard JCPDS and/or ICSD XRD database to determine the crystallographic phases of the sample. Data was also collected at Indian beamline, KEK, Japan and MCX beamline, Elettra, Italy.

Two Dimensional X-Ray Diffraction (2D-XRD)

Two-dimensional x-ray diffraction (XRD [6]) refers to x-ray diffraction applications with two-dimensional (2D) detector and corresponding data reduction and analysis. The two-dimensional diffraction pattern contains more information than a one-dimensional profile collected with the conventional diffractometer in PXRD. From Figure 2.5, we see the general difference between two diffraction tools. The diffraction data collection in the conventional diffractometer is confined within a plane, here referred to as diffractometer plane. With a 2D detector, the measurable diffraction is no longer limited in the diffractometer plane. Instead, the whole or a large portion of the diffraction rings (as called Debye ring) can be measured simultaneously. The conventional diffraction pattern, collected with either a scanning point detector or a linear PSD, is a plot of X-ray scattering intensity at different $2\theta$ angles. The 2D diffraction pattern contains far more
information then the conventional diffraction pattern for applications, such as: Phase ID; Percent Crystallinity; Particle Size and Shape; Texture; and Stress [7]. 2D-XRD data were collected at ID09 beamline, ESRF, France (see Figure 2.6).

### 2.2.3 X-ray Absorption Spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is a widely used technique in determining the electronic and local chemical structures of a given system [8].

It is also termed as X-ray Absorption Fine Structure in short XAFS. In 1913, Maurice de Broglie measured first absorption edge. Around 1920, Fricke observed fine structure above X-ray absorption edges. In 1930, Kronig proposed a LRO theory based on crystal periodicity; then a SRO theory to explain EXAFS in GeCl$_4$ molecule. In 1970, Sayers, Stern, and Lytle gave modern theory, FT of EXAFS. It is very versatile.
technique as it can be used in almost all form of sample (solid/liquid) to understand its local structure.

The basic principle is based on the interaction of the high energy x-ray with the core level electrons of the particular element of the sample under investigation. The samples are exposed to variable energy x-ray beam, monochromatized from a continuous spectrum of photon beam generated in synchrotron radiation. During the energy scan the absorption of the photon beam occurs when the energy equals to the binding energy of the electrons sitting at a core level and a jump in the spectrum is observed. This absorption is measured and analyzed to extract the local chemical and electronic structures. The whole spectra region are divided into two different zones in the energy scale, namely, the x-ray absorption near edge structure (XANES), and the extended x-ray absorption fine structure (EXAFS) (see Figure 2.8). The rising edge of the spectra termed as $E_0$ is equivalent to the binding energy of the element at energy level under investigation.

![XANES and EXAFS](image)

**Figure 2.8:** A typical x-ray absorption spectrum at Fe K-edge taken at XAFS beamline Elettra, Italy.

The XAS is measured either through the fluorescence yield, where the emitted photons are detected in transmission mode or in fluorescence mode, or total electron yield, where the current through the sample connected via the ground is
measured, depending on the nature of sample (see Figure 2.7). We have measured XAS through transmission and fluorescence mode only. The samples were mixed well with matrix provided, we used polyvinylpyrrollidine (PVP) and graphite in most cases, and a pellet was prepared from it. These pellets were mounted in the sample holder and data was collected. For fluorescence mode, samples were casted directly in a CA membrane and mounted in sample holder. All the data were collected several times to confirm the reproducibility.

**X-ray Absorption Near Edge Spectroscopy (XANES)**

XANES is the initial feature of the XAS spectra, which arise as soon as the energy of the x-ray matches with one of the core-level energies of an atom of a sample. It comprises of the pre-edge, edge and just the end of post-edge. The electron from core-level escapes after absorbing the photon which creates a hole at the core-level. This core hole is then filled up by an electron from a higher energy level. In this process a photon is released which can further be absorbed to release another electron, termed as Auger electron. As XANES is an element specific phenomena, many details of the electronic structure can be investigated, e.g. the valency, the chemical environment (crystal field environment), etc. By using the polarized photon beam one can probe the type of orbitals (e.g. s, p, d, dxy, dz2 etc.) of a particular atom.

**Extended X-ray Absorption Fine Structure (EXAFS)**

EXAFS is a very powerful structural local probe, which does not require a long-range order. The oscillatory part, after the post-edge (i.e. few eV to 1000 eV from the absorption edge) of an element is analyzed in EXAFS. This region gives information about chemical environment of the probed element in terms of the number (co-ordination number) and types of its neighbors, interatomic distances,
chemical disorder etc. The oscillation above the absorption edge is caused due to interference phenomena (see Figure 2.9). The photoelectrons emitted from an absorber atom are back scattered by the neighboring atoms and produce a backward wavefront of electrons. This back scattered wave interfere with the forward wave and for a particular energy of the photoelectrons the constructive interference occurs, which results in a local maxima in the absorption spectrum. As energy increases of the incident x-ray, the wavelength of the photoelectron becomes smaller and for a particular wavelength destructive inference occurs, which is reflected as a local minima in the absorption spectra and therefore, an oscillatory pattern is observed. The physical origin of EXAFS is thus electron scattering, and EXAFS can be thought of as a spectroscopically detected scattering method, rather than as a more conventional electron spectroscopy. The EXAFS signal is the purely oscillatory part of the absorption spectra, which can be expressed as,

\[ \chi(k) = \frac{\mu - \mu_0}{\mu_0} \]  

(2.2)

where, \( \mu \) is the absorption with the scatterer and \( \mu_0 \) is the absorption without

**Figure 2.9:** Formation of oscillation in typical EXAFS spectrum, due to interference.
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the scatterer. $\mu_0$ can not be measured directly, while it has been approximated by fitting. The amplitude of the oscillation is dependent on the number and type of scatterer atoms, while the wavelength depends typically on the absorber-scatterer distance. The shape of the spectra depends on the type of scatterer atoms and the phase depends on the absorber-scatterer potential over which the photoelectron moves. Therefore, all the information of the absorber and the scatterer atoms are stored in EXAFS spectra, which can be extracted by properly analyzing the collected data. The formula used in fitting is,

$$\chi(\kappa) = -S_0^2 \sum_j N_j \frac{F_j(\kappa)}{\kappa R_j^2} \exp(-2\sigma_j^2 \kappa^2) \sin(2\kappa R_j + 2\delta_{A,1}(\kappa) + \psi_j(\kappa))$$

(2.3)

where, $S_0$ is the reduction factor (depends on the absorber), $N_j$ is the number of neighboring atoms, $R_j$ is distance from central atom to the surrounding atom, $F_j$ is the Backscattering amplitude, $\kappa$ is EXAFS oscillation, $\sigma_j$ is the DW factor (thermal motion disorder), $\delta_{A,1}$ is phase shift of absorbing atom and $\psi_j$ is the phase shift of the scattering atom. EXAFS in principle does not require any particular experimental condition, such as vacuum. There are several types of sample-holders that allow collecting experimental data under varying temperature and pressure. Also the in-situ measurements can be performed very easily. Here, EXAFS measurement at As and Fe $K$-edge were performed at room temperature in transmission mode. The obtained pattern of EXAFS was extracted using Athena software and fitted using Artemis or ESTRA-Fit software.

2.2.4 X-ray Photoelectron Spectroscopy (XPS)

Photoelectric effect, the phenomenon in which photons incident on a material directly interact with core electrons of the atoms in that material and creates ionized states, emitting a photoelectron with a kinetic energy given approximately by the difference between the photon energy and the binding energy, this is the
basic principle utilized in photoelectron spectroscopy. This can be represented by the equation as,

\[ E_{KE} = E_{ph} - E_B - \phi \]  \hspace{1cm} (2.4)

here, \( E_{KE} \), \( E_{ph} \), \( E_B \) and \( \phi \) correspond to the kinetic energy of the ejected electron, energy of the absorbed photon, binding energy of the electron inside the atomic structure and the work function characteristic of the material, respectively.

A major step forward in photoelectron spectrometry was the work of Robinson (1923) and of Robinson and Young, in 1930 where they clearly observed the line shift caused by chemical bonding (chemical shift), which was the most important aspect for further applications of XPS. Next was the development of precision electron spectrometers by Steinhardt and Serfass at Lehigh University and above all in Uppsala University by Kai Siegbahn which led to the first XPS spectrum with high resolution in the 1950s. In later decades, Siegbahn’s group investigated core level binding energies and their shifts due to chemical bonding. Siegbahn coined the acronym ESCA (Electron Spectroscopy for Chemical Analysis), that includes Auger electrons besides photoelectrons, published a famous book with that title in 1967 and received the Nobel Prize in physics in 1981 for his achievements in ESCA. Auger electron spectroscopy (AES) was the first technique used for surface analysis of solids, followed by X-ray photoelectron spectroscopy (XPS).

Figure 2.10: Schematic diagram of x-ray photoemission spectrometer.
Chemical analysis of solid materials with electron spectroscopy is based on energy analysis of secondary electrons that are emitted as a result of excitation by photons \[9\]. The analyzer, hemispherical in shape, counts the electrons and measure their respective kinetic energy by means of several lens systems. During the data collection the samples are exposed to the x-ray beam generated from the x-ray gun. Main features of the techniques are, detection of all elements except hydrogen and helium, information of chemical bonding states and depth profiling in the nanometer region. In XPS, the sample surface is irradiated with photons of characteristic energy (usually Mg \(K\alpha\) or Al \(K\alpha\) radiation for lab source), which is kept in ultra high vacuum (UHV) (see Figure 2.10).

The measured photoelectron spectrum is a direct indication of the binding energies (see equation 2.4) of the different atomic electron levels. Usually the kinetic energy is plotted on the x-axis with increasing energy to the right, the binding energy increases from right to left. The inelastic mean free path of the photoelectrons is determined by the probability to suffer an energy loss, and the attenuation length (taking into account inelastic and elastic scattering) is determined by the probability of the photoelectron to be received by the electron energy analyzer. Kinetic energy of the electron and sample matrix determine and limit the information depth to the nanometer region. The XPS measurements can be performed by using both the synchrotron and laboratory based x-ray sources. The main advantage of using a synchrotron x-ray source is the high photon flux, which largely reduce the experimental time.

We have carried out XPS on our samples in lab based XPS instrument by Omicron, Germany and at Materials Science beamline, Elettra, Italy. The sample chamber was maintained below the pressure level of \(10^{-9}\) mbar to keep the sample surface clean as XPS is a highly surface sensitive probe. The sample were mixed with graphite and a pellet was made. This ensured conductivity and negated the effect of sample charging. In Elettra, samples were mounted on dual adhesive
carbon tape which ensured sample grounding.

2.2.5 Transmission Electron Microscopy (TEM)

Formed residues and nanoparticles synthesized exhibited sizes of only a few nanometers; which is beyond the resolution of naked eye, optical microscope and even usual scanning electron microscope. The most obvious technique used for this purpose is transmission electron microscopy (TEM). TEM gives most direct evidence of the size, shape and crystallinity of prepared nanoparticles. The electron and an optical microscopes have vastly different resolution powers that arise mainly because of the difference in wavelengths of the incident radiations used. Theoretically, the maximum resolution, $d$, that one can obtain with a light microscope has been limited by the wavelength of the photons ($\lambda$) that are being used to probe the sample and the numerical aperture of the system, $NA$.

$$d = \frac{\lambda}{2NA} \quad (2.5)$$

In TEM, electron speed approaches speed of light, thus modification of wavelength goes as follows:

$$\lambda_e \approx \frac{h}{\sqrt{2m_0E(1 + E/2m_0c^2)}} \quad (2.6)$$

where, $h$ is Planck’s constant, $m_0$ is the rest mass of an electron and $E$ is the energy of the accelerated electron and $c$ is the velocity of light.

The main components of the two microscopies are quite similar. In both cases, there exist a source that emits radiation (light/electron) and a condenser lens that focuses the beam onto the specimen. The beam after passing through the specimen is focused by an objective lens and intermediate image is formed, which is then magnified by projector lenses.
One of the major differences between optical and electron microscopes is that, in an optical microscope, the lenses are made up of glass and have fixed focal lengths, but an electron microscope requires magnetic lenses to bend electron and have a focal length that can be changed accordingly. At the top, the TEM consists of an emission source, which could be a tungsten filament, or a lanthanum hexaboride (LaB$_6$) source. It begins to emit electrons either by thermionic or field electron emission into the vacuum. The interaction of electrons with a magnetic field will cause electrons to move according to the right hand rule, thus allowing for electromagnets to manipulate the electron beam. Typically a TEM consists of three stages of lensing. The stages are the condenser lenses, the objective lenses, and the projector lenses. The condenser lenses are responsible for primary beam formation, whilst the objective lenses focus the beam that comes through the sample itself and the projector lenses are used to expand the beam onto the phosphor screen or other imaging device like CCD (see Figure 2.11). TEM image contrast arises due to the scattering of the incident beam by the specimen. When electron beam travels through the specimen, both its amplitude and its phase changes and both these kinds of changes can give rise to image contrast. Generally both these types of contrasts contribute to a TEM image, but one will dominate under a given experimental conditions. For that matter, TEM imaging are mainly divided into two categories, amplitude contrast imaging and phase contrast imaging [10]. Phase-contrast imaging is to an extent
synonymous with high resolution TEM where, the contrast in an image is generated from the difference in the phase of electron waves, scattered through a thin specimen. Whenever we refer to “fringes”, essentially we refer to a phase contrast phenomenon. These fringes in the image must correspond to an array of spots in the diffraction pattern of the specimen and can be related to each other via fast-Fourier-transformation (FFT). Similar to the way that the diffraction spots do not have any direct relation with the position of atom in the specimen; fringes in an image are not atomic planes. Thus lattice fringes are not the direct image of the structure, but give the lattice spacing information.

**Selected area electron diffraction (SAED):** High energy parallel electron beams when subjected to thin crystalline sample, the electrons passes through the sample easily and electrons are treated as wave-like rather than particle-like. Due to the high energy of the electrons the wavelength is a few thousandths of a nanometer where as the spacing between atoms in the sample is about 100 times larger. Therefore, the atom acts as a diffracting grating to the electrons and it is diffracted. Thus, the image formed will be series of spots, each spot corresponding to a diffraction condition of the nanocrystal under investigation. It is termed as “selected” as one can easily choose the part of the specimen from where the diffraction pattern is to be collected. This technique helps to identify crystal structure and examine crystal defects like XRD but in nanoscale.

**Scanning transmission electron microscope (STEM):** The difference between STEM with conventional TEM is that in STEM the electron beam is spotted on a narrow region and scanned over the sample in a raster. Thus it can generate elemental maps of any sample. By using a STEM and a high-angle detector, it is possible to form atomic resolution images where the contrast is directly related to the atomic number (z-contrast image).

**Energy dispersive X-ray spectrometry (EDS):** EDS makes use of the
X-ray spectrum to obtain localized chemical analysis of a sample. Both qualitative and quantitative analysis can be done by the identification and intensity measurement of the lines in the spectrum and is fairly straightforward owing to the simplicity of x-ray spectra.

**Elemental mapping:** Element map is showing the spatial distribution of the elements in a sample. The image is produced by progressively rastering the electron beam point by point over an area of interest.

In this thesis, the samples for TEM measurements were made by re-dispersing the particles in a suitable solvent followed by casting a small drop on a carbon coated Cu-grid. TEM images were taken on a JEOL-JEM 2010 electron microscopy using 200kV electron source. TEM images on STEM (HAADF) were taken on a UHR-FEG-TEM, JEOL; JEM 2100 F model using a 200 kV electron source.

### 2.2.6 Scanning Electron Microscopy (SEM)

The membranes morphology and thickness were checked by a SEM machine. In SEM a high energy electron beam (0.2 keV to 40 keV) is focused on the sample surface within a size of 0.5 to 5 nm by means of various focusing lenses. As the incident electron beams fall on the surface of sample the following phenomenon occurs, (i) the emission of the secondary electrons (SE) due to the inelastic scattering, (ii) back scattered electrons (BSE) due to the elastic scattering and (iii) electromagnetic radiation generated by the electronic transition from an excited atom. All of these emissions can be detected and mapped to produce an image of the sample surface. Imaging the sample surface by detecting the SE is the most commonly used technique for the topography of the surface.
In this technique low energy electrons ejected from the K-shell of the atoms by the inelastic scattering of the incident electron beam are collected by a detector, which is basically a scintillator photomultiplier. The electrons are accelerated to a high energy by high bias voltage that finally hits the scintillator to produce photons, which are further magnified by the photomultiplier and collected as a 2D intensity distribution generating the image. This intensity distribution is an one to one correspondence to the density of the SE. The density of SE is dependent on the atomic density and the interaction area between the beam and the sample surface. The density of SE are least when the beam is perpendicular to the surface as the exposed area becomes the smallest. Thus we see relatively darker image for a flat surface and brighter image for a inclined surface situated at the edge. This phenomena of SE makes the image topographically distinct.

We checked the sample morphology by means of a JEOL scanning electron microscope. Our main requirement was to identify if any pore is present on membrane surface along with its overall morphology. Thin slices of membrane samples were mounted perpendicularly to get an idea about the thickness of the membranes and to check if the structure was layered or not. A circular Cu slab
was used as the sample holder. Samples were mounted on the holder by conducting copper/carbon tape and a platinum coating was done over the sample surface in case the samples are insulating in nature in order to avoid the charging effect during the scan.

### 2.2.7 Flux Measuring Unit

Measurement of osmotic flux through the synthesized membranes were carried out in a home-made flux measuring unit [11], which was made using two peristaltic pump one for the feed side (pure water) and other for the draw side (1M NaCl solution). Both feed and draw water were constantly pumped in and out of the membrane module so that effect of external concentration polarization may be reduced. The membrane was placed in between the membrane module and was made water tight using O-ring and ring clamp (see Figure 2.13). Once the membrane was place in the module the temperature of the feed and draw was maintained at 20 °C, for the entire FO run. The gain in the weight in draw side due to movement of fresh water from the feed side via osmosis, was measured periodically in the weighing scale. The whole experiments were carried out for
72 hours uninterrupted. Periodically samples from both draw and feed side were collected and were quantified in ICP-OES for the amount of Na\(^+\) ions in feed or draw side. This gave us an idea about the dilution in draw side and reverse draw solute, if any, in the feed side.

### 2.2.8 Miscellaneous tools

Fourier Transform Infrared spectroscopy (FTIR) for membrane characterization. UV-visible-NIR absorption spectroscopy, Photoluminescence spectroscopy (PL) for nanorods characterization, Polarography, TDS meter, pH meter for natural water and synthetic water characterization were used periodically.
Bibliography


