Chapter II

MATERIALS AND METHODS

2. SYNTHESIS OF NANOPARTICLES

2.1 MATERIALS

To synthesize ZnS, ZnS:Cu\(^{2+}\), and surfactant capped ZnS:Cu\(^{2+}\), the following materials were used. All the glassware used in this experimental work was acid washed. The chemical reagents used were analytical reagent grade without further purification. Ultrapure water was used for all dilution and sample preparation. Zinc acetate Zn(C\(_2\)H\(_3\)O\(_2\))\(_2\), copper II acetate, sodium sulfide (Na\(_2\)S xH\(_2\)O), cetyl trimethylammonium bromide (CTAB, MW- 364.46), acetone, methanol and ethanol were obtained from S.D. Fine Chem. Ltd. Sodium hexametaphosphate (SHMP, MW- 611.8) was obtained from Loba Chemie. Pvt. Ltd. The n-trioctylphosphine oxide (TOPO, MW-386.65) was obtained from Alfa Aesar. All the chemicals are above 98% purity.

2.2 SYNTHESIS OF ZNS NANOPARTICLES

Zinc acetate dehydrate, hydrated sodium sulfide, were used without further purification. The ZnS:Cu\(^{2+}\) nanoparticles were synthesized by chemical precipitation method. The synthesis reaction was carried in the aqueous medium. Solutions of 0.5M Zn \((\text{C}_2\text{H}_3\text{O}_2)_2\), and 0.5M Na\(_2\)S were prepared individually in 50 ml de-ionized water. First, the Zn\((\text{C}_2\text{H}_3\text{O}_2)_2\) solution is stirred very well for 25-30 minutes at 80°C. Next, 50 ml of Na\(_2\)S solution was added drop by drop to the above solution.
Immediately a white precipitate appeared. The precipitate was collected from the solution by adding a known volume of acetone. Immediate flocculation of nanoparticles occurred. To remove the last traces of adhered impurities, the particles were washed thrice using de-ionized water, ethanol and acetone. The washed particles were dried at 80°C in air for 2hrs.

2.3 SYNTHESIS OF ZnS:Cu$^{2+}$ NANOPARTICLES

The ZnS nanoparticles doped with different Cu$^{2+}$ concentrations were synthesized in water without using other agent. In a typical experiment, 5.48g (0.5M) of Zn (CH$_3$COO)$_2$.2H$_2$O in 50 ml aqueous and copper acetate in 25 ml aqueous with different concentrations (0.2, 0.4, 0.6, 0.8 and 1%) were mixed drop by drop. The concentration of Cu$^{2+}$ was adjusted by controlling the quantity of copper acetate in the above mixture. The mixture was stirred magnetically at 80°C until a homogeneous and colourless solution is obtained. Then, 2.75 g of 50 ml Na$_2$S was added drop by drop to the above mixture. After the Na$_2$S injection, a white voluminous precipitate appeared. It slowly dissolved under formation of ZnS: Cu$^{2+}$ nanoparticles during incubation under stirring for 30 min at 80°C. During the incubation time, the pH slowly increased from 3.7 to 7.5. The obtained dispersions looked transparent and were purified by dialysis against de-ionized water and ethanol several times to remove impurities. The products were dried in hot air oven at 80°C for 2hrs.
2.4 SYNTHESIS OF SURFACTANTS CAPPED ZnS:Cu$^{2+}$

NANOPARTICLES

The surfactants ZnS:Cu$^{2+}$ nanoparticles were prepared with zinc acetate, copper acetate and sodium sulfide precursors. The soluble surfactants were used as stabilizing agents. Different concentrations of soluble surfactants were prepared individually in 50 ml of distilled water using magnetic stirrer to completely dissolve. Following the same synthesis steps (in section 2.3), newly prepared surfactants were added into zinc acetate before adding copper acetate with continuous stirring. Then, following the other steps continuously (in section 2.3), surfactant capped ZnS:Cu$^{2+}$ nanoparticles were synthesized. Thus obtained nanoparticles were washed three times using distilled water. Washing was carried out to remove the byproducts and the excessive surfactants that were bound with the nanoparticles. After washing, the nanoparticles were dried at 80°C for 2hrs. During drying, complete conversion of surfactants capped ZnS:Cu$^{2+}$ takes place. Figure 2.1 presents a schematic of the formation of surfactants capped ZnS:Cu$^{2+}$ nanoparticles.
2.4.1 The following are various surfactants with different concentrations used for the particle syntheses:

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Trioctylphosphine oxide ([\text{CH}_3(\text{CH}_2)_7]_3\text{PO}) ((\text{TOPO}))</td>
<td>0.5, 1.0, 1.5, 2.0 ((\text{g}))</td>
</tr>
<tr>
<td>2. Sodium hexametaphosphate ((\text{NaPO}_3)_6) ((\text{SHMP}))</td>
<td>0.5, 1.0, 1.5, 2.0 ((\text{g}))</td>
</tr>
<tr>
<td>3. Cetyl trimethylammonium bromide((\text{C}<em>{19}\text{H}</em>{42}\text{NBr})) ((\text{CTAB}))</td>
<td>0.5, 1.0, 1.5 ((\text{g}))</td>
</tr>
</tbody>
</table>

Fig 2.1 A schematic of the formation of surfactants - capped ZnS:Cu\(^{2+}\) nanoparticles
2.5 CHARACTERIZATION

The synthesized particles were characterized using various techniques. The techniques include X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). The elemental composition on the surfaces of nanoparticles was monitored by SEM-EDX. The TEM and SEM were used to obtain the morphological information of nanoparticles. Size of the particles was measured using particle size analyzer. XRD and TEM were used to identify the crystalline phases and crystal sizes of the ZnS:Cu$^{2+}$ nanoparticles. The presence of different functionalities on the capping agents and their retention on nanoparticle functionalization could be characterized by Fourier transform infra-red spectrometer (FT-IR). The UV-vis spectrophotometer was used to measure the excitation and band gap of the samples. The emission spectra were recorded by photoluminescence spectrometer (PL). Electron spin resonance spectroscopy (ESR) was used to identify the doping ion in ZnS. Thermo graviometric analysis (TGA) were performed to study the thermal properties of ZnS:Cu$^{2+}$ nanoparticles.

2.5.1 UV-VIS AND PHOTOLUMINESCENCE

2.5.1.1 UV - Vis

UV-Visible absorption spectroscopy involves the spectroscopy of photons in the UV-Visible region. This means it uses light in the visible,
near ultraviolet (UV) and near infrared (NIR) ranges. The absorption in the visible ranges directly affects the color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy. The fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

Absorption of light by solution is one of the oldest and still one of the more useful instrumental methods. Absorption of visible and ultraviolet (UV) radiation is associated with excitation of electrons, in both atoms and molecules, to higher energy states. All molecules will undergo electronic excitation following absorption of light, but for most molecules very high energy radiation (in the vacuum ultraviolet, <200 nm) is required. However for molecules containing conjugated electron systems, light in the UV-Visible region is adequate. As the degree of conjugation increases, the spectrum shifts to lower energy.

Beer-Lambert Law: The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/VIS spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration.
2.5.1.2 Photoluminescence (PL)

Luminescence is defined as a phenomenon in which the electronic state of a substance is excited by some kind of external energy (physical or chemical) and the excitation energy is given off as light (Shionoya and Yen (1999)). The fluorescence studies are generally concerned with two types of spectrum, the excitation spectrum and emission spectrum. The excitation spectrum is determined by measuring the emission intensity at a fixed wavelength while varying the excitation wavelength. The emission spectrum is determined by measuring the variation in emission intensity wavelength for the fixed excitation wavelength. The difference between the excitation and emission wavelengths is called as Stoke's shift. PL can be divided into two types, phosphorescence and fluorescence.

Photoluminescence in solids is a process in which luminescence is stimulated by the interaction of photons (electromagnetic radiation) with a material. The process is divided into two major types, namely intrinsic and extrinsic photoluminescence (Wolf and Deubel, 1997). Intrinsic photoluminescence is observed in materials which contain no impurity atoms. Extrinsic photoluminescence is caused by intentionally incorporated impurities and in most cases metallic impurities or defects (Yang, 2003d, Wolf and Deubel, 1997).

2.5.1.2.1 Intrinsic photoluminescence Studies

There are three kinds of intrinsic photoluminescence; namely band-to-band, exciton and cross-luminescence. Band-to-band results
from the recombination of an electron in the conduction band with a hole in the valence band and can only be observed in a very pure crystals at relatively high temperatures (Wolf and Deubel, 1997). An exciton is a composite particle of an excited electron and hole interacting with one another. Cross-luminescence is produced by the recombination of an electron in the valence band with a hole in the outermost core band. It can only take place when the energy difference between the top of the valence band and that of the outermost core band is smaller than the band-gap energy; otherwise, an Auger process occurs (Wolf and Deubel, 1997).

2.5.1.2.2 Extrinsic photoluminescence Studies

Most of the observed types of luminescence that have practical applications belong to this category. Intentionally incorporated impurities are called activators and materials made luminescent in this way are called phosphors. Extrinsic luminescence is classified into two types, namely localized and delocalized luminescence. In a delocalized luminescence the excited electrons and holes of the host lattice participate in the luminescence process, while in the case of the localized luminescence the excitation and emission processes are confined in a localized luminescence center, the host lattice does not contribute to luminescence process (Wolf and Deubel, 1997).

2.5.2 SAMPLING PROCEDURE AND INSTRUMENTS USED

The prepared samples were dispersed in de-ionized water. Then UV-Visible and photoluminescence spectra were recorded using de-
ionized water as a reference. The absorbance and fluorescence spectra of the samples contained in 1cm² cuvette were scanned immediately after preparing the solution. The UV-Vis spectra of as prepared nanoparticles were recorded in the wavelength range of 200 - 600 nm. The spectra were observed in de-ionized water and pure solvents were used as references. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 600 nm. Photoluminescence spectra were recorded in different ranges, which depend on excitation wavelength.

Absorption spectral measurements were carried out with a Hitachi Model U–2001 UV–Vis spectrophotometer and fluorescence measurements were made using a JASCO FP – 550 spectrofluorimeter. (accuracy = ±1.5nm and range – 220 to 750 nm)

2.5.3 DTA AND TGA CHARACTERIZATION

Differential thermal analysis or DTA is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DTA analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The main application of DTA is in studying phase transitions, such as melting, glass transitions, or
exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DTA with great sensitivity. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential thermal analysis is able to measure the amount of heat absorbed or released during such transitions. DTA may also be used to observe more subtle phase changes, such as glass transitions. DTA is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing. DTA is more sensitive to phase transition temperature (with a precision of 0.01°C) and is capable of monitoring the exact rate of energy exchange or reaction rate. Positions of all these peaks depend on heating rate. Increasing the heating rate caused every peak shift towards higher temperatures, with the first two endothermic peaks merged into a broad one. This is due to activation energy involved in such transition.
Thermo gravimetric analysis or TGA is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to show the point at which weight loss is more apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

TGA is commonly employed in research and testing to determine the characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation. The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with the sample. The pan is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument.

Analysis is carried out by raising the temperature gradually and plotting weight against temperature. A method known as Hi-res TGA is
often employed to obtain greater accuracy in areas where the derivative curve peaks. In this method, temperature increase slows as weight loss increases. This is done so that the exact temperature at which a peak occurs can be more accurately identified (Hobart Willard et al., 1986 and Khandpur (2001)).

2.5.3.1 Sampling procedure and Instrument used

The sample holder has two cavities, one for sample and other for the reference material. Normally it is made up of different materials in different shape and size depending upon the nature of the substance to be studied and amount of the sample used. The sample holder itself should not undergo any transformation and interact with the sample. A large ratio yields better stabilization of heat, it acts as an insulator for heat flow between the two materials. When the ratio is smaller, it reduces the absorption of heat by the block and increases the sharpness of the peak. Generally, sample holder made up of platinum is employed.

Here the Differential Thermal Analysis (DTA) and Thermo graviometric analysis (TGA) of the sample were done by SDT Q600 V20.9 Build 20 (Thermal Analysis Instruments, Inc.) with a resolution of ±0.01mg. The sample was taken in a Platinum crucible and heated from 0 to 1000°C and heating rate is maintained at 10°C/min using air as a medium under static condition.
2.5.4 X-RAY DIFFRACTION

X-ray diffraction (XRD) is an efficient analytical non-destructive technique used to investigate structural properties of crystalline materials. It is also used in applications such as phase identification, determination of grain size, composition of solid solution, lattice constants, and degree of crystallinity in a mixture of amorphous and crystalline substances (Cao, 2004). A diffraction pattern is produced when a material is irradiated with a collimated beam of X-rays. The X-ray spectra generated by this technique provide a structural fingerprint of the material (unknown). The relative peak height is generally proportional to the number of grains in a preferred orientation and peak positions are reproducible (Cao, 2004). The intensity of the diffracted X-rays is measured as a function of diffraction angle 2θ and the specimen orientation.

2.5.4.2 Crystallite size measurement

Phase identification using x-ray diffraction depends on the position of the peaks in a diffraction profile as well as the relative intensities of these peaks to some extent. Another aspect of diffraction from material is of importance to consider how diffraction peaks are changed by the presence of various types of defects such as small number of dislocations in crystals with dimensions of millimeters. Smaller grain size can be considered as another kind of defect and can change diffraction peak widths. Very small crystals cause peak broadening. The crystallite size is easily calculated as a function of peak width.
specified as the full-width of half maximum peak intensity (FWHM), peak position and wavelength using Debye Scherrer’s equation (0.9λ/βcosθ).

2.5.4.3 Determination of lattice parameters

For the wurtzite structure the interplanar distance \(d\) of \(\{hkl\}\) plane is related to the lattice parameters \(a\) and \(c\) via the Miller indices \(hkl\):

\[
\left( \frac{1}{d_{hkl}} \right)^2 = \frac{4}{3} \left[ \frac{i^2}{a^2} + \frac{j^2}{b^2} + \frac{k^2}{c^2} \right] + \frac{r^2}{c^2}
\]

Hence, the lattice parameters can be calculated using the interplanar distance \(d\) and \(hkl\) value.

2.5.4.4 Sampling procedure and Instrument used

X-ray diffraction analysis was performed on ZnS:Cu nanopowder at room temperature. During the recording of the diffractogram, a narrow slit of 0.1 mm was used with a scanning speed of 0.02 /sec. The sample was firmly pressed into an aluminium holder, with an area of 10mm. The diffraction patterns were obtained over the \(2\theta\) value in the region of \(20^\circ\) to \(80^\circ\) at a scan step time of 10.3356 (s). The estimated error is the lattice parameter of the order of 0.005Å. The experimental pattern was compared with patterns obtained from JCPDS database.

The X-ray diffraction (XRD) patterns of selected samples were recorded using X’pert PRO diffractometer. Cu Kα radiation (\(\lambda=1.54060\text{Å}\)) was used for recording the samples at room temperature. The X-ray tube was operated at a voltage of 40 kV and a current of 30 mA.
2.5.5 SCANNING ELECTRON MICROSCOPY (SEM) WITH EDX

2.5.5.1 SEM

Scanning electron microscopy (SEM) is a technique whereby a beam of energetically well-defined and highly focused electrons are scanned across a material (sample). The microscope uses a lanthanum hexaboride (LaB₆) source and is pumped using turbo and ion pumps to maintain the highest possible vacuum. The technique can provide materials (only conducting and semiconducting) information about topography, morphology and crystallography (http://www.unl.edu/CMRAcfem/semoptic.htm). If the system is equipped with energy dispersive x-ray spectrometer (EDX), it can also provide information about chemical composition of the material (http://nue.clt.binghamton.edu/semtem.html). The basic principle of the system is that, the electron beam impinges the surface and generates a splash of electrons with kinetic energies much lower than the primary incident electrons called secondary electrons. An image of the sample surface is constructed by measuring the secondary electron intensity as a function of the primary beam position. The SEM has many advantages over traditional microscopes. It has a large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, so closely spaced specimens can be magnified at much higher levels. Because the SEM uses electromagnetic lenses, the researcher has much more control in the degree of magnification. All of these advantages, as well as the actual strikingly clear images, make the
scanning electron microscope one of the most useful instruments in research today (http://www.purdue.edu/REM/rs/sem.htm 2008). All the samples, whether simple or complex, must meet certain basic requirements before they can be viewed in SEM.

(1) They must be prepared to an anhydrous state.

(2) They must be secured to a substrate suitable for the particular sample.

(3) They must be minimally conductive to avoid problems of charging. Methods by which these requirements are fulfilled can vary according to the nature of the sample (Walker, 1978).

2.5.5.2 Energy Dispersive X-ray Spectroscopy (EDX)

Energy dispersive X-ray spectroscopy (EDS or EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. This type of spectroscopy relies on the investigation of the sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles (Yurugi, et al., 1993). Its characterization capabilities are due to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from each other. To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons or a beam of X-rays, is focused on the sample being studied. At rest, an atom within the sample contains ground state (or unexcited)
electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray.

The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. The energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted. This allows the elemental composition of the specimen to be measured. The amount of energy released by transferring the electrons depend on which shell it is transferring from, as well as which shell it is transferring to.

Furthermore, the atom of every element releases X-rays with unique amounts of energy during transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established.

The output of an EDX analysis is an EDX spectrum. The EDX spectrum is just a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single
element. The higher a peak in a spectrum, the more concentrated the element is in the specimen.

An EDX spectrum plot not only identifies the element corresponding to each of its peaks, but also the type of X-ray to which it corresponds. The most significant issue to note from this is that the X-rays generated from any particular element are characteristic of that element, and as such, can be used to identify which elements are actually present under the electron probe. This is achieved by constructing an index of X-rays collected from a particular spot on the specimen surface, which is known as a spectrum.

2.5.5.3 Sampling procedure and Instrument used

Powder samples of nanoparticles are studied by SEM-EDX. The surface of the sample has been stubbed using the double-side adhesive carbon tape. Samples are coated with the help of gold coater (JEOL Auto Fine coater model JFC-1600, Coating time is 120 seconds with 20 mA) and deposited with a thin layer gold (heavy metal) on the sample. The specimen is now ready for SEM-EDX observation.

The microphotographs of these samples were recorded using JEOL SEM model, JSM-5610 LV with an accelerating voltage of 20KV, at high vacuum mode (HV) and secondary electron image (SEI). Using the OXFORD INCA Energy Dispersive X-ray analysis (EDX), weight percentage of major elements present in the samples was determined.
2.5.6 TRANSMISSION ELECTRON MICROSCOPY

Theory

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is transmitted through a specimen, and then an image is formed. The image is then magnified and directed to appear either on a fluorescent screen or layer of photographic film, or to be detected by a sensor such as a CCD camera. The system can study small details in the cell or different materials down to near atomic levels (Wang et al., 2003, http://en.wikipedia.org/wiki/Transmission_Electron_Microscopy). It can investigate the size, shape and arrangement of the particles which make up the specimen as well as their relationship to each other on the scale of atomic diameters. Materials to be analyzed with this technique need to have dimensions small enough to be electron transparent and that can be produced by the deposition of a dilute sample containing the specimen onto support grids. The suspension is normally a volatile solvent such as ethanol, ensuring that the solvent rapidly evaporates allowing a sample that can be rapidly analyzed.

The possibility for high magnifications has made the TEM a valuable tool in medical, biological and material sciences research. In all cases, the specimens must be very thin and able to withstand the high vacuum present inside the instrument. For biological specimens, the maximum specimen thickness is roughly 1 micrometer (http://en.wikipedia.org/wiki/Transmission_Electron_Microscopy). To withstand the instrument vacuum, biological specimens are held at
liquid nitrogen temperatures. In material science/metallurgy, the specimens tend to be naturally resistant to vacuum and must be prepared as a thin foil, or etched so that some portion of the specimen is thin enough for the beam to penetrate.

The system can also be used for the determination of the electron diffraction patterns of the crystalline structures. A crystalline material interacts with the electron beam mostly by diffraction rather than absorption. The intensity of the transmitted beam is affected by the volume and density of the material through which it passes. The intensity of the diffraction depends on the orientation of the planes of atoms in a crystal relative to the electron beam. At certain angles the electron beam is diffracted strongly from the axis of the incoming beam, while at other angles the beam is largely transmitted.

2.5.6.1 Sampling procedure and Instrument used

For sample preparation, dilute drops of suspension were allowed to dry slowly on carbon-coated copper grids for TEM measurement. The sample was kept in desiccator prior to an investigation.

In this study, the structure, size and images of ZnS:Cu\textsuperscript{2+} nanoparticles were obtained using a Philips CM 200 Transmission Electron Microscopy. Operating voltage of the TEM is 20-200 kV and resolution is 2.4Å. TEM images are formed using transmitted electrons (instead of the visible light) which can produce magnification details up to 1,000,000X. The images can be resolved over a fluorescent screen or a photographic film.
2.5.7 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

Fourier Transform Infrared (FTIR) spectroscopy is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gases (http://mmrc.caltech.edu/FTIR/FTIRintro.pdf). The wavelength of light absorbed is characteristic of the chemical bond as can be seen from the spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectroscopy does not require a vacuum, since neither oxygen nor nitrogen absorbs infrared rays.

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by absorbing light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E_0) and the first excited state (E_1)] http://www.thermo.com.cn/Article.aspx?ID=187). The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalorie/mole
which corresponds to the infrared portion of the electromagnetic spectrum.

FTIR can provide following information:

- It can identify unknown materials.
- It can determine the quality or consistency of a sample.
- It can determine the amount of components in a mixture.

FTIR spectroscopy was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed.

2.5.7.1 Sampling procedure and Instrument used

The standard Potassium Bromide (KBr) pellet technique is most commonly employed as a sampling technique for FT-IR absorption measurements of solid material. The same technique has been adopted for the present work.

Materials required for KBr pressed pellet method are Potassium Bromide (KBr), Acetone, die for making KBr pellets, laboratory hydraulic press for confined sample, small hand agate mortar and pestle and mechanical vacuum pump.
To remove the moisture absorbed by KBr powder, pure KBr has been dried at 120°C-150°C for about 6 hours. Complete removal of water has been confirmed by recording the FTIR spectrum of pure KBr. Then fine grained samples were mixed with pure KBr in the ratio of 1:30 and then the mixture was pressed under vacuum at about 10 tones by placing the mixture in 13 mm diameter die to get a disc of about 13mm diameter and 1mm thickness. All the spectra were recorded in the region 4000-400cm⁻¹.

The FTIR spectra of uncapped and different surfactants capped ZnS:Cu nanoparticles were obtained on an AVATOR 360 spectrometer. The instrument has accuracy of ± 0.01cm⁻¹ and resolution of ± 4 cm⁻¹. The instrument was calibrated with the spectra of a standard polystyrene film at room temperature. Every time, before the spectrum of the sample was taken; the spectrum of the standard polystyrene film was obtained and checked for the accuracy and transmittance

2.5.8 ELECTRON SPIN RESONANCE (ESR)

Electron spin resonance is a branch of absorption spectroscopy in which radiation having frequency in the microwave region is absorbed by paramagnetic substances to induce transitions between magnetic energy levels of electrons with unpaired spins. In ESR spectroscopy, the two different energy states are produced due to the alignment of the electron magnetic moments relative to the applied field and a transition between these two energy takes place upon the absorption of a quantum of radiation in the microwave region. One of the most important uses of
ESR technique lies in the detection of extremely short-lived (transient) free radical intermediates in chemical reactions. The ESR spectroscopy has been widely employed in the study of chemical, photochemical and electro chemical reactions which proceed via free radical mechanisms, because of the occurrence of hyperfine structure, which is the result of interaction between the unpaired electrons and magnetic nuclei in the paramagnetic species. In many cases, hyperfine structure enables unambiguous identification of the species (Sharma, 2003).

2.5.8.1 Sampling procedure and Instrument used

The method is very rapid and can be measured in aqueous solution over the range from $10^{-6}$ M to 0.1 M. Powder samples were diluted in the reference solution.

The ESR spectra of Cu$^{2+}$ doped ZnS nano particles were recorded on a Bruker EMX Plus spectrometer employing 100 kHz modulation at a TE$_{102}$ mode cavity. The modulation amplitude was 0.1mT peak to cavity. The standard DPPH was used to calibrate the applied magnetic field settings.

2.5.9 PARTICLES SIZE ANALYZER

Particles size analyzer (PSA) measures the sizes of grains or particles in a sample very quickly. They use methods such as light scattering, sedimentation, laser diffraction etc., to calculate particle sizes. It provides data on particle size distributions, which is used in many industries.
Microtrac has been a pioneer in particle sizing technology for over 35 years. The Nanotrac is the latest generation of dynamic light scattering sub-micron analyzers from Microtrac. The enhanced design on the Nanotrac features are faster measurements (up to 20 times faster), smaller particle size capability (to 0.8 nm), higher precision, higher accuracy and advanced software capabilities in a small, robust dynamic light scattering instrument with no moving components.

2.5.9.1 The Controlled Reference Method

Particles suspended in a dispersing fluid are subjected to random collisions with the thermally excited molecules of the dispersing fluid resulting in Brownian motion. The velocity and direction of the resulting motion are random but the velocity distribution of a large number of mono-sized particles averaged over a long period will approach a known functional form, in these cases of the size distribution of the particles.

2.5.9.2 Sampling procedure and Instrument used in the particle

Highly diluted sample is used to characterize the particles size analyzer. Sample required is typically less than 3ml in standard cell or 0.2ml with small cell option. Particles size was analyzed at room temperature. The samples were dispersed in water to form as fluid.
Nanotrac Specifications Model Nanotrac NPA 150 was used having the measurement capability of 0.8 to 6500 nm. The resolution of the instrument is 0.01 nm. Run time for analysis is 120 second. Particles of the ZnS:Cu$^{2+}$ sizes were recorded.