CHAPTER II

MATERIALS AND METHODS

ABSTRACT

The synthesis procedure of pure ZnO, ZnS, CdS nanoparticles and ZnO/CdS/ZnS, ZnS/ZnO/CdS core-shell nanocomposites are given. Also the details of characterization techniques such as UV-Vis, PL, TG-DTA, XRD, SEM and TEM, are briefed. The preparation of samples for these techniques is given.
CHAPTER II

MATERIALS AND METHODS

2.1 MATERIALS

To synthesize uncoated (ZnO, CdS and ZnS) and multilayer coated ZnO/CdS/ZnS, ZnS/ZnO/CdS nanocomposites, the following materials were used. Ultrapure water was used for all dilution and sample preparations. Zinc acetate dehydrate \( [\text{Zn} \ (\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}] \), cadmium acetate \( (\text{Cd} \ (\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}) \), sodium sulfide \( (\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}) \), sodium hydroxide and ethanol obtained from Nice Chemical company were used as precursors. All the chemicals are above 98% purity. All the glassware’s used in this experimental work were acid washed. The chemical reagents used were of analytical reagent grade without further purification.

2.2 SYNTHESIS OF ZnS, CdS AND ZnO NANOPARTICLES

The ZnS, CdS and ZnO nanoparticles were synthesized in aqueous medium at an air atmosphere. In a typical experiment, to synthesis ZnS, 5.48 g (0.5 M) of Zn \( (\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} \) in 50 ml aqueous and an equal molar amount of sodium sulfide in aqueous were mixed drop by drop. The mixture was stirred magnetically at 80°C until a homogeneous solution was obtained. After 1 h at room temperature, a white precipitate was appeared. To synthesis of CdS nanoparticles, 0.1 M of cadmium acetate in 50 ml and equal molar amount of Na\(_2\)S was added drop by drop to the above solution under stirring at 80°C. After the Na\(_2\)S injection, a yellow voluminous precipitate was appeared. ZnO was synthesized by mixing of 0.5M of zinc acetate and 1M of sodium hydroxide solution during vigorous stirring. After two hour continues stirring, white precipitate was formed. The obtained dispersions were washed by de-ionized water and ethanol several times to remove impurities. The products were dried in a hot air oven at 120°C for 2 h.
2.3 SYNTHESIS OF ZnO/CdS/ZnS NANOCOMPOSITES

In a typical procedure, 0.5 M of Zn (CH$_3$COO)$_2$·2H$_2$O in 50 ml of deionized water and an 1M of sodium hydroxide in deionized water were mixed drop by drop. The mixture was stirred magnetically at 80°C until a homogeneous white solution was obtained. After 30 min, 50 ml cadmium acetate solution (0.1–0.5 M) were added to the above solution drop by drop. Subsequently, sodium sulfide solution (0.1–0.5 M) was added drop by drop into the above solution. After the injection of sodium sulfide, white colour solution was slowly changed into green yellow colour solution. It may be due to the formation of the ZnO/CdS in the colloidal solution. Yellow colour precipitate was appeared after 2h at room temperature.

After that, zinc acetate solution (0.1–0.5 M) was added to the above colloidal solution. Then, the same molar amount of sodium sulfide solution was added drop by drop with continuous stirring to the above solution. Consequently, the green yellow colour was slowly changed into light yellow colour solution. This dictates the formation of the ZnO/CdS/ZnS nanocomposites. Then, the precipitate was collected and washed several times with deionized water and ethanol and then dried in a hot air oven at 120°C for 4 h. The synthesized ZnO/CdS/ZnS nanocomposites were characterized using different techniques.

2.4 SYNTHESIS OF ZnS/ZnO/CdS NANOCOMPOSITES

In a typical procedure, 0.5M of Zn (CH$_3$COO)$_2$·2H$_2$O in 50 ml of deionized water and an equal molar concentration of sodium sulfide in deionized water were mixed drop by drop. The mixture was stirred magnetically at 80°C until a homogeneous white solution was obtained. After 30 min, 50 ml of zinc acetate solution (0.1–0.5 M) were added to the above solution. Subsequently, 50 ml of sodium hydroxide solution (0.1–0.5 M) was added drop by drop into the above solution. After the
injection of sodium hydroxide, a bright white colour solution was obtained. It may be due to the formation of the ZnS/ZnO in the colloidal solution. After 30 min continuous stirring, 50 ml of cadmium acetate solution (0.1–0.5 M) was added to the above colloidal solution. Then, the same molar amount of sodium sulfide solution was added drop by drop with continuous stirring to the above solution. Consequently, the green colour was slowly changed into green yellow colour solution. This dictates the formation of the CdS layer on ZnS/ZnO nanocomposites.

Then, the precipitate was collected and washed several times with deionized water and ethanol and then dried in a hot air oven at 120°C for 4 h. The synthesized ZnS/ZnO/CdS nanocomposites were characterized using different techniques.

2.5 CHARACTERIZATION

The X-ray diffraction (XRD) patterns of the powdered samples were recorded using XPERT PRO diffractometer with a Cu Kα radiation (λ = 1.54060 Å). The crystallite size was estimated using the Scherer equation for the major XRD peak. The morphology and size of the nanoparticles were studied using TEM (Technai 20G2, FEI) microscope. The optical absorption spectra of the all samples in de-ionized water were recorded using UV-1650PC SHIMADZU spectrometer. Fluorescence measurements were performed on a RF-5301PC spectrophotometer. Emission spectra were recorded under the different excitation wavelengths at room temperature. Thermal properties of the synthesized samples were investigated through Thermo gravimetric analysis-Differential thermal analysis (TGA-DTA).

2.5.1 UV-Vis and Photoluminescence

2.5.1.1 UV-Vis

Ultraviolet and visible spectroscopy has been widely used for the characterization of nanomaterials and the techniques can generally be
categorized into two groups: absorption and emission spectroscopy and the vibrational spectroscopy. The former determines the electronic structure of atoms, ions, molecules or crystals through exciting electrons from the ground to excited states (absorption) and relaxing from the excited to ground state (emission). The vibrational techniques may be summarized as involving the interaction of photons with species in a sample that results in energy transfer to or from the sample via vibrational excitation or de-excitation. The ultraviolet (UV) region scanned normally from 200 to 400 nm and the visible portion is from 400 to 800 nm.

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 the concentration of the solution.

The expression of Beer-Lambert law is

\[ A = \log \left( \frac{I_0}{I} \right) = ECL \]

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 (cm)

\( E = \) molar absorptive

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.
2.5.1.2 Photoluminescence (PL)

Photoluminescence abbreviated as PL is a process in which a substance absorbs photons and then re-radiates photons. Quantum mechanically, this can be described as an excitation to a higher energy state and then return to lower energy state accompanied by the emission of photon. Luminescence is the spontaneous emission of light from the excited electronic states of physical systems. The emission is preceded by the process of excitation, which may be produced by a variety of agents. If it is achieved by the absorption of light it is called photoluminescence, if by the action of an electric field electroluminescence, if by a chemical reaction chemiluminescence, and so on.

Photoluminescence is an important process for measuring the purity and crystalline quality of semiconductors. In PL, one measures physical and chemical properties of materials by using photons to induce excited electronic states in the material system and analyzing the optical emission as these states relax. It is a contact less non destructive method of probing the electronic structure of materials.

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. 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, 2003).

2.5.1.2.1 Intrinsic photoluminescence

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. 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.

2.5.1.2.2 Extrinsic photoluminescence

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 a case of the localized luminescence the excitation and emission processes are confined in a localized luminescence centre, the host lattice does not contribute to luminescence process.

2.6. 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 1cm$^2$ 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 range, which depends on excitation wavelength.
Absorption spectral measurements were carried out with UV-1650PC SHIMADZU spectrometer and fluorescence measurements were performed on a RF-5301PC spectrophotometer.

2.7 X – RAY DIFFRACTION (XRD)

X – Ray diffraction (XRD) is a versatile, non – destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and synthetic materials.

The beginning of X –ray diffraction from crystals was developed by Max Von Laue in 1912 and few years later, W. L. Bragg came up with the idea of treating diffraction from a crystal as reflection from the lattice planes, each of which is identified with a set of integers h, k and l. These numbers are known as Miller indices. Miller indices help in identifying the planes from which reflection takes place. The interference of the beam of X – rays reflected from successive parallel planes corresponding to particular triad of hkl values, leads to diffraction effects. Thus, the regular’s arrangement of atoms in the cleavage planes of a crystal might provide a grating element suitable to diffract X – rays. Thus, X - rays diffraction permits the observation of the interior of solids, which help in understanding and predicting different properties of solids. The crystal structure can be studied through the diffraction of electrons, neutrons and photons.

2.7.1 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 the diffraction from material is the 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. Small size of 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 \(0.9\lambda/\beta\cos\theta\).

\[2.7.2\] Sampling procedure and Instrument used

X-ray diffraction analysis was performed for the synthesised samples 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 20 value in the region of 20° to 80° at a scan step time of 10.3356 (s). The estimated error is the lattice parameter is of the order of 0.005 Å. The experimental pattern was compared with patterns obtained from JCPDS database.

The X-ray diffraction (XRD) patterns 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 operated at a voltage of 40 kV and a current of 30 mA.

\[2.8\] TRANSMISSION ELECTRON MICROSCOPY (TEM)

Today TEM constitute arguably the most efficient and versatile tools for the characterization of materials. After the discovery of the electron by J.J. Thomson in 1897, Max Knoll and Ernst Ruska in 1932 found a way to propel electrons through a sample to create an image in a way similar to optical microscopy. The technique quickly surpassed the resolution of optical microscopy and in 1938 the first commercial instrument began to be produced by Siemens-Halske Company in Berlin.

The transmission electron microscopy is a technique whereby a
beam of electrons is transmitted through an ultra thin specimen (less than 200 nm) interacting with the specimen as they pass through. An image is formed from the interaction of the electrons transmitted through the specimen, which is magnified and focused onto an imaging device, such as a fluorescent screen or on a layer of film or to be detected by a sensor such as a camera (CCD).

The diffraction pattern and image are formed at the back focus plane and image plane of the objective lens. If we take the back focus plane as the objective plane of the intermediate lens and projector lens, we will obtain the diffraction pattern on the screen. It is said that the TEM works in diffraction mode. If we take the image plane of the objective lens as the objective plane of the intermediate lens and projector lens, we will form image on the screen. It is the image mode (Shah and Tokeer Ahmad, 2010).

2.8.1 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 uncoated and multi shell coated nanocomposites were obtained using a Technai 20G2, FEI Transmission Electron Microscopy. Operating voltage of the using TEM is 20-200kv and resolution is 2.4 Å. 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.

2.9 SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructure morphology and chemical composition for
nanomaterials. SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interaction reveal information about the sample including external morphology (texture), chemical composition, crystalline structure and orientation of materials making up the sample. 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. Samples must be solid and they must fit into the microscope chamber. Maximum size in horizontal dimensions is usually of the order of 10 cm, vertical dimensions are generally much more limited and rarely exceed 40 nm. For most instruments samples must be stable in a vacuum of the order of $10^{-5} - 10^{-6}$ torr.

2.9.1 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 JSM-5610LV with INCA EDS. Coating time is 120 seconds with 20 mA) and deposited with 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 30KV, at high vacuum mode (HV) and secondary electron image (SEI).
2.9 THERMO GRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS (TG-DTA)

2.9.1 Thermo Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). TGA can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption and desorption. Likewise, it can provide information about chemical phenomena including chemisorptions, dehydration, decomposition and oxidation (Coats and Redfern, 1963).

Thermogravimetric analysis relies on a high degree of precision in three measurements: mass change, temperature, and temperature change. Therefore, the basic instrumental requirements for TGA are a precision balance with a pan loaded with the sample, and a programmable furnace. The furnace can be programmed either for a constant heating rate, or for heating to acquire a constant mass loss with time.

TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture). TGA can be used to evaluate the thermal stability of a material. In a desired temperature range, if a species is thermally stable, there will be no observed mass change. Negligible mass loss corresponds to little or no slope in the TGA trace. TGA also gives the upper use temperature of a material. Beyond this temperature the material will begin to degrade.
2.9.2 Differential Thermal Analysis (DTA)

Differential thermal analysis is the most widely used and is probably a very suitable method for the identification and estimation purposes especially in the case of soils (clays) and minerals. The chemical or physical changes which are not accompanied by the change in mass on heating are not indicated in thermogravimetric but there is a possibility that such changes may be indicated in DTA. Differential thermal analysis is a technique in which the temperature of the substance under investigation is compared with the temperature of a thermally inert material such as alumina and is recorded with furnace temperature as the substance is heated or cooled at a predetermined uniform rate.

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 are 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. Since 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 toward higher temperatures, with the first two endothermic peaks merged into one broad one. This is due to activation energy involved in such transition.

2.9.3 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. Here the Differential Thermal Analysis (DTA) and Thermo gravimetric 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.

2.9.4 Tauc Plot Method

A Tauc plot is a convenient way of displaying the optical absorption spectrum of a material pioneered by J. Tauc (1968), who proved that momentum is not conserved even in a direct optical transition. The optical band gap of the nanoparticles is calculated using the Tauc’s relation $a \alpha = A (h \nu - E_g)^n$. Where $h \nu$ is the incident photon energy, $\alpha$ is the optical absorption co-efficient, $A$ is constant and $n$ is the exponent that determines the type of electronic transition causing the absorption and can take the values 1/2 and 2 depending whether transition is direct or indirect respectively. The best linear relationship is obtained by plotting $(\alpha h \nu)^2$ against $h \nu$. The value of the band gap is determined from the intercept of the straight line at $\alpha = 0$. 

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CHAPTER III

OPTICAL, STRUCTURAL AND MORPHOLOGICAL STUDIES OF ZnO, CdS AND ZnS NANOPARTICLES