CHAPTER-2
SYNTHESIS AND CHARACTERIZATION OF MODIFIED METAL OXIDES
AND METAL SULPHIDES NANOPARTICLES

Nanoparticles have recently attracted significant attention from the science community. Nanoparticles with diameters in the range of 1 to 20 nm, promise to play a significant role in developing technologies. They exhibit unique physical properties that give rise to many potential applications in areas such as nonlinear optics, luminescence, electronics, catalysis, solar energy conversion, and optoelectronics. Modified metal oxide and metal sulphides nanostructure materials have unique size dependent chemical and physical properties that render them applicable in the emerging field of medicine, solar cell\textsuperscript{120}, antibacterial agents\textsuperscript{121}, geological materials\textsuperscript{122}, etc. The introduction of impurity atom into semiconducting nanomaterial is primary for controlling the properties of semiconductor such as band gap or electrical conductivity. The band gap energy and surface area of nanoparticles increases with decreasing particle size. Hence, nanosized semiconductor particles can possess photo redox properties with reduction reactions which might not otherwise proceed in bulk materials, being able to occur readily using sufficiently small particles therefore used as photocatalysts, and catalysts in organic transformations\textsuperscript{123}.

This chapter focused the attention on synthesis of cheaper, ecofriendly, reusable, effective metal oxide, metal sulphide, doped metal oxides, doped metal sulphide nanoparticles catalyst for the photodegradation of organic dyes, and organic transformations. Their structure and morphology were characterized by UV-DRS, IR, X-ray diffraction, SEM, EDAX, TEM, SAED, ESR, PL, TGA, and BET surface area measurement method.
This chapter is further divided in four sections

**Section A:** Synthesis and characterization of semiconducting PbO and Ni doped PbO nanoparticles

**Section B:** Synthesis and characterization of semiconducting CdO and Cs doped CdO nanoparticles

**Section C:** Synthesis and characterization of semiconducting PbS and Co doped PbS nanoparticles

**Section D:** Synthesis and characterization of semiconducting ZnS and Sm doped ZnS nanoparticles
Section-A

Synthesis and Characterization of Semiconducting PbO and Ni Doped PbO Nanoparticles

2.1A. Introduction:

Metal oxides play a vital role in many areas of chemistry, physics, and materials science. These metals are able to form a large diversity of oxide compounds, and have number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence the structural characteristics, the lattice symmetry, and cell parameters. These nanomaterials have attracted a great deal of attention from researchers of various fields due to their numerous technological applications such as control of NO_x emissions from automotive engines, removal of other environmental pollutants, catalysts, sensors, supercapacitors, lubricants, biological applications, and adsorbers. The wurtize phase is essential in catalysis applications, e.g. TiO_2, WO_3, and SnO_2 have been used as catalysts but it possesses poor catalytic activity. The oxides like MgO, SiO_2 are found to be inactive since most metal oxide, and sulphides cannot be reused hence such photo conductors are not suitable for long term treatment processes.

Lead oxide (PbO) is a member of the relatively small family of lead (II) binary oxides. Lead oxide (PbO) nanomaterials itself has two forms, red α PbO (litharge) which is stable at low temperature, and yellow β PbO (massicot) which is stable at high temperature. The α PbO phase transformation to β PbO takes place at about
and both are photoactive semiconductors with band gaps of 1.92 eV and 2.7 eV. Lead oxide is an important industrial material due to its unique electronic, optical and mechanical properties, its potential applications in functionalized materials and nanodevices, lead acid batteries, and lithium secondary batteries. Due to its high power density, wide application temperature range, complete recycling system, relatively low price electro deposition used in deposition onto precious metals, lead oxide-matrix composite, high pressure phase transformation, oriented lead oxide on silica, biomedical applications, and Pb (II) selective electrode. Due to unique property of PbO it is used as modifiers in luminescent glassy materials, gas sensors, paints, and pigments. Recently, lead oxide nanoparticles used in studying electron structure of insulator metal interface.

Due to simplicity of design, low cost of manufacturing, reliability, relative safety there is a high interest to improve characteristics of lead oxide to obtain more discharge capacity, and more cycle life. Therefore, research to improve discharge capacity of lead oxide is still in demand. After the doping of nickel ion into lead oxide nanoparticles, the interactions between the lead oxide, and nickel ion may change the electronic properties of PbO which results in the further enhancement of discharge capacity. Lead oxide nanoparticles have been synthesized by several physicochemical methods including, spray pyrolysis, thermal decomposition, selected control synthesis, sonochemical, synthesis by coordination polymers, pulsed current electrochemical method, microwave irradiation, sol-gel, soft template synthesis, and hydrothermal method.

Today the chemical synthesis is one of the important techniques for nanocrystalline materials. It can be performed using a range of precursor and synthesis conditions such as temperature, time, and concentration. Variation of these
parameters leads to different size, surface morphology, and geometries of resulting materials. The organic dyes are one of the main environmental contaminants due to their toxic and non biodegradable nature. Although these organic dyes are present in very low amounts in industrial effluents, they have shown ample potential to disturb the environment. These dyes are insufficiently removed by conventional sewage treatment plants due to their high biochemical stability, water solubility, and high molecular weight. Therefore, there is a need of new technology which is more efficient, consume less energy, environmental benign protocol for the clean, and green environment. In order to achieve a better solution for this problem, and application of lead oxide nanoparticles as a catalyst in organic transformations, the lead oxide nanoparticles were synthesized using hydrothermal method. Nickel doped lead oxide nanoparticles were also synthesized to extend the light absorption spectrum of lead oxide nanoparticles towards the visible region.

Transition metal ion (nickel) encapsulation enhances the interfacial charge transfer reaction of lead oxide and decrease the crystallite size of lead oxide nanoparticles. The goal of this study is to investigate the effect of nickel ion doping on the catalytic activity of lead oxide nanoparticles. The synthesized lead oxide (PbO), and nickel ion doped lead oxide nanoparticles is characterized by using different analytical techniques like UV-visible diffused reflectance (UV-DRS), Fourier-transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy dispersive analysis of X-ray (EDAX), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), electron spin resonance spectroscopy (ESR), photoluminescence spectroscopy (PL), and BET surface area measurements technique.
2.2A. Experimental:

The starting materials lead nitrate (Sigma Aldrich, 99.0 %), citric acid (Loba Chemie, 99.5 %), methanol (Loba Chemie, 99.5 %), nickel sulphate (Sigma Aldrich, 99.0 %), and sodium hydroxide (Sigma Aldrich, 98.5 %) were used as reactants for the synthesis of PbO and Ni doped PbO nanoparticles. Double distilled water was used throughout the experiment.

2.2.1A. Synthesis of PbO nanoparticles:

An aqueous solution of citric acid (2.5 mol) was added to a magnetically stirred methanolic solution of lead nitrate (2.0 mol) at room temperature, then the reaction mixture was stirred well over 20 minutes. The aqueous solution of sodium hydroxide was added slowly and stirred until solution becomes alkaline. The complex formation was obtained as a precipitate and it was stirred for another 2 hrs at room temperature. The white solid product obtained was filtered, washed thoroughly with distilled water for the complete removal of nitrate, and hydroxide ion. The precipitate was dried in oven at 110°C for 2 hrs and ground mechanically to fine powder. The resulting dry powder was calcinized at 500°C for 2 hrs at the rate of 2°C per minute. The calcinized PbO used for further characterization.

2.2.2A. Synthesis of Ni doped PbO nanoparticles:

The synthesized lead oxide (PbO) nanoparticles were used as precursor material, and nickel sulphate (NiSO₄) as dopant. A lead oxide nanoparticle (1.0 mol) was mixed with 3 % and 7 % NiSO₄ solution along with sodium hydroxide solution (1 N, 10 ml). The slurry obtained was stirred well, transferred into Teflon autoclave and kept in oven at 110°C for 20 hrs. The precipitate obtained was vacuum filtered, washed with distilled water for the removal of soluble impurities, and dried at 110°C.
for 2 hrs. These samples were calcinized at 500°C for 2 hrs, these calcinized 3 % and 7 % Ni doped lead oxide nanoparticles are used for characterization.

The UV-visible diffuse reflectance spectra (UV-DRS) were recorded using diffuse reflectance UV-visible spectrophotometer (Shimadzu UV-2450 diffuse reflectance mode) using BaSO₄ as a reflectance standard. Photoluminescence (PL) spectrum at room temperature was recorded by Perkins Elmer spectrophotometer by using Xenon arc lamp (λ = 325 nm) as the light source. Infra red spectra were run on a 8400s Shimadzu FT-IR spectrophotometer as KBr pellets. The X-ray diffraction (XRD) patterns were recorded on a multipurpose X-ray diffractometer (Philips-1710 diffractometer CuKα, λ = 1.5406 Å) at a scan rate of 0.17° 20 sec⁻¹. The scanning electron microscopy (SEM), and energy dispersive analysis of X-rays (EDAX) was carried out by using scanning electron microscope (JEOL JEM-6360A model) equipped with JEOL JEC-560 auto carbon coater SEM. The transmission electron microscopy (TEM) images recorded with selected area electron diffraction (SAED) using CM-200 Philips Microscope. The thermal stability was studied by thermogravimetric analysis (TGA) using Perkins Elmer, USA instrument at heating rate of 0.01°C-100°C per minute in the temperature range from room temperature to 1000°C. An electron spin resonance (ESR) spectrum was recorded on E-112 EPR spectrometer VARIAN, USA. The Brunauer, Emmet, and Teller (BET) surface area was recorded with the help of Quantachrome Autosorb Automated gas sorption system.

2.3A. Results and Discussion:

2.3.1A. UV-DRS analysis:

Figure 2.1 depicts the UV-visible diffused reflectance spectra (UV-DRS) of the nanocrystalline PbO, 3 %, and 7 % Ni doped PbO nanoparticles. It shows broad
band at 396, 402, and 407 nm for PbO, 3 %, and 7 % Ni doped PbO nanoparticles respectively. The blue shift arises from that of bulk PbO due to quantum confinement effects. The band shifted to higher wavelength with increase in the amount of the dopant. The band gap energies obtained by using UV-DRS of the synthesized PbO, 3 %, and 7 % Ni doped PbO nanoparticles are 3.13, 3.08, and 3.04 eV respectively on the basis of equation\(^{157}\), \(E_g = \frac{1239.8}{\lambda}\), where \(\lambda\) is the wavelength (nm) of the exciting light.

These results reveals that after the encapsulation of nickel ion in synthesized PbO nanoparticles, the absorption goes in the visible region in comparison with undoped PbO nanoparticles. It means that the doped metal oxide nanoparticles are sensitive to visible light. The shifting of band is arising due to doping effect on band gap of semiconducting PbO nanoparticles. The photocatalytic activity of nickel doped PbO nanoparticles is greatly enhanced due to increased photo generation rate of charge transfer between \(\text{Ni}^{2+}\) electrons and the PbO nanoparticles conduction band to valence band\(^{158}\).

### 2.3.2A. FT-IR analysis:

The FT-IR spectra for the synthesized PbO, 3 %, and 7 % Ni doped PbO nanoparticles in KBr matrix is shown in Fig. 2.2. The broad band at 498.2 cm\(^{-1}\) in PbO is associated with the vibration of Pb-O bond\(^{159}\). There is a broad band with very low intensity at 3446.4 cm\(^{-1}\) corresponds to the stretching vibration of the OH group and it may be due to small amount of water adsorbed on the surface of PbO nanoparticles\(^{160}\). The band at 1408.7 cm\(^{-1}\) is due to the -OH deformation vibration of water molecule. The water is in dissociated form because no band at 1640.2 cm\(^{-1}\), which is characteristic of the deformation vibration of water adsorbed in the molecular form. Further, careful inspection of FT-IR spectra shows strong absorption band at
498.2 cm$^{-1}$ indicates presence of $\beta$ PbO (massicot) form of PbO synthesized nanoparticles. The bands at 920.1 cm$^{-1}$ and 1047.6 cm$^{-1}$ of very low intensities attributed due to oxygen stretching and bending frequency. In 3 % and 7 % Ni doped PbO nanoparticles the bands at 920.1 cm$^{-1}$ and 1047.6 cm$^{-1}$ are more pronounced due to the presence of nickel ion.

2.3.3A. X-ray diffraction (XRD) analysis:

The XRD pattern of synthesized PbO, 3 %, and 7 % Ni doped PbO is shown in Fig. 2.3. The diffraction peaks indicate the nanocrystalline nature of synthesized powder. It shows peaks at an angle 29.1, 30.4, 32.5, 37.7, 49.4, 50.9, 53.3, 56.2, and 63.7 corresponds to the reflection from 111, 002, 200, 210, 022, 220, 222, 311, and 131 crystal planes respectively. The XRD pattern is an agreement with the orthorhombic structure of PbO (JCPDS Card No. 76-1796) with a space group Pca $2_1$ (29). Sharp diffraction peak indicates good crystallinity of PbO nanoparticles, and the broadening of peaks indicates that the particles are of nanometer size. The XRD pattern of 3 % and 7 % Ni doped PbO sample is almost coincide with that of pure PbO, it can be found that nickel doping do not change crystalline structures of PbO nanoparticles. It indicates that nickel is present in ionic state bonded with oxygen of the PbO inside the frame work. The average particle size was calculated using Debye-Scherrer’s equation$^{162}$.

The XRD data shows that the particle size of synthesized PbO is 69 nm, 64 nm for 3 % Ni doped PbO, and 61 nm for 7 % Ni doped PbO nanoparticles. It shows that the average particle size of PbO nanoparticles with increase in amount of dopant and this method produce the fine particles. In comparison with pure PbO nanoparticles sample the nickel encapsulated PbO nanoparticles have relatively small particle size indicating that the doping can improve the morphology, and retard the grain growth.
Fig. 2.1: UV-DRS spectra of synthesized PbO, and (3 %, and 7 %) Ni doped PbO

Fig. 2.2: FT-IR spectra of synthesized PbO, and (3 %, and 7 %) Ni doped PbO

Fig. 2.3: XRD pattern of synthesized PbO, and (3 %, and 7 %) Ni doped PbO
of PbO nanoparticles. This may be due to the fact that dopant ions inhibit crystal growth, and sintering between grains during the heat treatment, Pb$^{+2}$ atoms in crystal lattice is replaced by Ni$^{+2}$ ions.

2.3.4 A. SEM and EDAX analysis:

Figure 2.4 represents SEM images of synthesized PbO, 3 %, and 7 % Ni doped PbO nanoparticles. The crystal morphology of the particles is quite similar to each other, and likely become spongy discrete particle nature. The SEM image shows that the synthesized PbO, 3 %, and 7 % Ni doped PbO materials are agglomerates. However, the size of the particles varies in the range of 69 to 61 nm as measured using the XRD patterns. The EDAX analysis of synthesized PbO, 3 %, and 7 % Ni doped PbO materials are shown by Fig. 2.4. Strong peaks of Pb and O are found in the EDAX spectrum, and detectable amounts of nickel indicate that nickel ion has doped into PbO nanocrystallites. It indicates that 2.97 % and 6.94 % of nickel ion is present in the doped PbO nanoparticles. The slight decrease in the amount of nickel is due to the leaching of unbound nickel ion during the washing.

2.3.5A. TEM and SAED analysis:

The particle size and crystal morphological information of the sample was further investigated by TEM, SAED analysis, and are depicted in Fig. 2.5. The TEM image of PbO, 3 %, and 7 % Ni doped PbO nanoparticles shows that the orthorhombic structure with agglomerate nature. Moreover, the particle size of the sample obtained from TEM analysis is comparable to those estimated from Debye-Scherrer equation and varies in the range of 69 to 61 nm. The dark spot in the TEM micrograph can be associated with synthesized PbO, 3 %, and 7 % Ni doped PbO nanoparticles as SAED pattern associated with such spots reveals the occurrence of PbO, 3 %, and 7 % Ni doped PbO nanoparticles in total agreement with the XRD
Fig. 2.4: SEM and EDAX of a) synthesized PbO, b) 3 % Ni doped PbO, and c) 7 % Ni doped PbO
data. The SAED pattern of PbO, 3 %, and 7 % Ni doped PbO nanoparticles shows similar d-values as obtained by XRD data.

2.3.6A. Thermogravimetric analysis (TGA):

Figure 2.6 shows the TGA curve of synthesized PbO nanoparticles before the calcination process. It reveals that the thermal decomposition takes place up to 450°C. The decomposition of hydrocarbon takes place in this temperature range. From 450°C to 600°C temperature region the material are stable, and it shows stability of the synthesized material.

2.3.7A. Electron spin resonance (ESR) analysis:

Interaction of nickel ion and the host PbO semiconducting nanoparticles studied by ESR spectrum and is shown in Fig. 2.7. This technique has been used to characterize the environment of the paramagnetic species in host lattice of different species. The ESR signal of 3 % Ni doped PbO nanoparticle was recorded at room temperature. The ESR spectrum characterization indicates that the doping of transition metal (nickel) is homogeneous, and there is no secondary phase present. The ESR signal also shows that the effective ‘g’ factor is greater than 2 (2.00277) indicates a clear evidence of ferromagnetism in this synthesized materials. This ‘g’ value also used to determine the number of unpaired electrons in the molecule.

2.3.8A. Photoluminescence analysis (PL):

The photoluminescence spectrum of synthesized PbO is shown by Fig. 2.8, which exhibits a broad blue emission band at 473 nm (2.62 eV) and strong green-yellow emission band around 500 nm (2.48 eV). The visible band arises due to the defects in PbO nanostructures. The peak at 473 nm is probably caused due to, i) transition from monovalent interstitial lead (Pb\(^{+2}\)) or oxygen vacancy (V\(_{o}\)) to the monovalent vacancy (V\(_{o}^{+}\)), and ii) transition from conduction band to the monovalent
Fig. 2.5: TEM, and SAED of a) synthesized PbO, b) 3 % Ni doped PbO, and c) 7 % Ni doped PbO
Fig. 2.6: TGA curve of synthesized PbO nanoparticles

Fig. 2.7: ESR spectra of 3 % Ni doped PbO nanoparticles

Fig. 2.8: PL spectrum of synthesized PbO nanoparticles
vacancy ($V_{o}^+\). The origin of blue emission from the undoped PbO nanoparticles is associated with the intrinsic defect centers such as oxygen vacancy ($V_{o}^0\) lead vacancy or the oxygen interstitial vacancy.

2.3.9A. BET surface area analysis:

The BET surface area measurement analysis of synthesized PbO, 3 %, and 7 % Ni doped PbO nanoparticles are shown by Fig. 2.9. The N$_2$ adsorption-desorption isotherms, and BJH pore size distribution of PbO nanoparticles reveals that the prepared sample have typical IV N$_2$ adsorption-desorption isotherms with H$_1$ hysteresis. The BJH pore size distribution demonstrates that all the samples have a narrow pore diameter range. Using N$_2$ adsorption-desorption isotherm the specific surface area ($S_{BET}$) of PbO, 3 %, and 7 % Ni doped PbO nanoparticles are 29.38 m$^2$/g, 31.99 m$^2$/g, and 34.32 m$^2$/g respectively. The average pore volumes ($V_p$) were 0.01889 cc/g, 0.02256 cc/g, and 0.02386 cc/g for PbO, 3 %, and 7 % Ni doped PbO nanoparticles respectively. The pore diameter (dp) was 24.63 Å, 24.77 Å, and 30.86 Å for PbO, 3 %, and 7 % Ni doped PbO nanoparticles respectively.

The specific surface area ($S_{BET}$) increases from undoped PbO to Ni doped PbO nanoparticles, and also increase with increase in the concentration of the dopant. The results reveal that the Ni doped PbO nanoparticles have high surface area, so it act as efficient catalyst in heterogeneous catalysis and photodegradation of various organic dyes. In catalysis greater the surface area of the catalyst, the faster the reaction will proceed because catalytic action takes place at a surface$^{164}$.
Fig. 2.9: BET surface area, and pore size of a) synthesized PbO, b) 3 % Ni doped PbO, and c) 7 % Ni doped PbO
Section-B

Synthesis and Characterization of Semiconducting CdO and Cs Doped CdO Nanoparticles

2.1B. Introduction:

The semiconductor nanoparticles belong to state of matter in the transition region between molecules and bulk solids in which the relevant dimension changes\textsuperscript{165}. Nanocrystalline materials are attracting much attention due to their increasing applications in solar energy conversion, non-linear optics, heterogeneous catalysis, microelectronics, and photocatalysis\textsuperscript{166}. Cadmium oxide (CdO) nanomaterial is an II-VI $n$-type of semiconductor with a direct band gap of 2.5 eV\textsuperscript{167} and 1.98 eV an indirect band gap\textsuperscript{168}. The difference in band gap originates from cadmium, oxygen vacancies, and strongly depends on the method of synthesis\textsuperscript{167}. In nanocrystalline size affects the spacing between energy levels which becomes the cause of increase of energy gap. The equilibrium and dynamic properties of nanomaterials are completely different with their bulk materials.

The optical transmittance of CdO in the visible region of the spectrum has very low value\textsuperscript{169}. It has interesting properties such as large band gap, low electrical resistivity, and high transmission in the visible region. Cadmium oxide nanoparticles have unique physical properties that are size, and shape dependent due to which it is useful for a wide range of applications such as photo transistors, solar cells, lithium ion batteries, transparent electrodes, photodiodes, and gas sensors\textsuperscript{170}. A cadmium oxide nanoparticle has distinguished properties\textsuperscript{171} and is widely used as a transparent conductive oxide (TCO) in optoelectronic devices\textsuperscript{172}, nonlinear materials\textsuperscript{167}, and catalysts\textsuperscript{173}. The modified CdO nanoparticles are used as sensor for the study of
biological active compounds\textsuperscript{174}. A cadmium oxide nanoparticle is transparent conducting oxide material with high carrier mobility, and has great potential in optoelectronic devices\textsuperscript{175}.

Nanostructured materials are attracting a great deal of attention due to their ability for achieving specific process, selectivity in biological, and pharmaceutical applications\textsuperscript{176}. Nanoparticles antimicrobial formulations could be used as effective bactericidal materials\textsuperscript{177}. Based on the metal ions, the nanomaterials exhibit broad spectrum of biocidal activity towards different bacteria, fungi, and viruses\textsuperscript{178}. The effect of nanoparticles on bacteria is very important since they have low level, and hence enter the food chain of the ecosystems\textsuperscript{179}. Cadmium oxide nanomaterials have been reported for antibacterial properties and used as an antibacterial agents\textsuperscript{180}. Cadmium oxide nanoparticles are non toxic, chemically stable under high temperature, and capable of photocatalytic oxidation\textsuperscript{181}. The cadmium oxide nanocrystalline materials also used as catalyst in organic transformation like acylation of alcohols, phenols, and amines\textsuperscript{182}.

The physical and chemical properties of cadmium oxide nanoparticles are relative to its stoichiometry as well as particle size, shape which depend on its preparation methods, and condition\textsuperscript{183}. Cadmium oxide nanoparticles have been synthesized by several physicochemical methods including, sol-gel method\textsuperscript{184}, thermal evaporation\textsuperscript{171}, chemical bath deposition\textsuperscript{185}, vapour transport\textsuperscript{186}, solid-vapour deposition\textsuperscript{187}, precipitation method\textsuperscript{188}, photosynthesis using flowers extract\textsuperscript{189}, solvothermal method\textsuperscript{190}, mechanochemical reaction\textsuperscript{191}, solid state synthesis\textsuperscript{192}, microemulsion method\textsuperscript{180}, sonochemical\textsuperscript{193}, and hydrothermal method\textsuperscript{194}. The physical and chemical properties of cadmium oxide nanomaterials were improved by modifying the synthesis methods\textsuperscript{195}. Hydrothermal method can be a beneficial
technique to prepare various nanostructures among the other methods so that more researchers prefer it\textsuperscript{196}.

Cadmium oxide nanoparticles has not only unique optical, and optoelectrical characteristics but also has the selective catalytic properties that can be used for photodegradation some of the organic compounds, dyes, pigments, and many of environmental pollutants\textsuperscript{197}. So in order to remove such dyes, environmental pollutants, and to bring organic transformations using CdO nanoparticles, we synthesize the CdO nanoparticles, and Cs doped CdO nanoparticles by hydrothermal method. The metal doped CdO nanoparticles have large grain size as compared to undoped CdO nanoparticles\textsuperscript{198}. Therefore, the catalytic activity of the CdO nanoparticles was improved by doping the cesium ion into it.

Keeping above aspects in view, we report in this section the synthesis of CdO and Cs doped CdO fine nanostructured photocatalyst. The composition and crystallinity of these materials have been determined by using different analytical techniques including, UV-DRS, PL, FT-IR, XRD, SEM, EDAX, TEM, SAED, TGA, and BET surface area measurements technique.

2.2B. Experimental:

All chemicals used were of analytical grade and used without further purification. The starting materials cadmium chloride (Sigma Aldrich, 99.9 %), triton X-100 (Qualigens, 99.0 %), methanol (Loba Chemie, 99.5 %), cesium nitrate (Sigma Aldrich, 99.9 %), and sodium hydroxide (Sigma Aldrich, 98.5 %) were used for the synthesis of CdO and Cs doped CdO nanoparticles.

2.2.1B. Synthesis of CdO nanoparticles:

A triton X-100 as a capping agent (0.05 mol) was added to a magnetically stirred methanolic solution of cadmium chloride (1.0 mol) at room temperature then
the reaction mixture was stirred well over 20 mins. The aqueous solution of sodium hydroxide (1.0 N) was added slowly and stirred until solution becomes alkaline. The complex formation was obtained as a precipitate and it was stirred for another 2 hrs at room temperature. The white solid product obtained was filtered, washed thoroughly with distilled water for the complete removal of chloride, hydroxide ion, and to remove the soluble impurities. The precipitate was dried in oven at 110°C for 2 hrs, and ground mechanically to fine powder. The resulting dry powder was calcinized at 400°C for 4 hrs at the rate of 2°C per minute. These calcinized cadmium oxide (CdO) nanoparticles are used for characterization.

2.2.2B. Synthesis of Cs doped CdO nanoparticles:

The synthesized cadmium oxide (CdO) nanoparticles were used as precursor material, and cesium nitrate [Cs (NO₃)₂] as dopant for the synthesis of Cs doped CdO nanoparticles. Initially cadmium oxide (1.0 mol) nanoparticles were mixed with 3 %, and 7 % cesium nitrate solution along with sodium hydroxide solution (1.0 N, 10 ml). The slurry obtained was stirred well, and transferred into Teflon autoclave, and kept in oven at 110°C for 20 hrs. The precipitate obtained was vacuum filtered, washed with distilled water for the removal of soluble impurities, and dried at 110°C for 2 hrs. These samples were calcinized at 400°C for 2 hrs. These calcinized 3 %, and 7 % Cs doped cadmium oxide are used for further characterization.

2.3B. Results and Discussion:

2.3.1B. UV-DRS analysis:

The UV-visible diffused reflectance spectra of the nanocrystalline CdO, 3 %, and 7 % Cs doped CdO nanoparticles are shown in Fig. 2.10. The spectra show broad bands at 340, 346, and 353 nm for CdO, 3 %, and 7 % Cs doped CdO nanoparticles respectively. The blue shift observed as compared to bulk CdO is due to quantum
confinement effects. With increase in the amount of the dopant, the band position shifted to higher wavelength side. The band gap energies of the synthesized CdO, 3 %, and 7 % Cs doped CdO nanoparticles are 3.64, 3.58, and 3.52 eV respectively. The shifting of band is arising due to doping effect on band gap of CdO semiconducting nanoparticles.

2.3.2B. FT-IR analysis:

Figure 2.11 depicts FT-IR spectra for the synthesized CdO, 3 %, and 7 % Cs doped CdO nanoparticles in KBr matrix. The absorption bands at 3523 cm\(^{-1}\) are attributed to the stretching vibration of the OH group due to small amount of water adsorbed on the surface of CdO nanoparticles\(^{160}\). The strong broad absorption band at about 1408 cm\(^{-1}\) is due to the asymmetric stretching vibrations of water molecule\(^{192}\). The broad absorption band at 858 cm\(^{-1}\) shows presence of Cd-O bond\(^{199}\). The FT-IR spectra shows absorption band at 501 cm\(^{-1}\) also confirms the presence of Cd-O bond\(^{200}\) and frequency at 1000 cm\(^{-1}\) due to oxygen stretching. The absorption band at 501 cm\(^{-1}\) becomes broad due to the presence of cesium ion in CdO nanoparticles.

2.3.3B. X-ray diffraction (XRD) analysis:

Figure 2.12 shows XRD pattern of synthesized CdO, 3 %, and 7 % Cs doped CdO nanoparticles. The diffraction peaks indicate the nanocrystalline nature of synthesized materials, and peaks at 20 values of 15.4, 17.2, 29.4, 31.06, 35.08, 38.7, 39.5, and 43.06 corresponds to the reflection from 111, 200, 311, 222, 400, 331, 420, and 422 crystal planes. The XRD pattern is in agreement with cubic structure of CdO nanoparticles (JCPDS card no. 02-1102) indicated the formation of cadmium oxide phase. Sharp diffraction peak indicates good crystallinity of CdO nanoparticles and all XRD patterns show obvious size broadening effects, due to small crystallite size. It can be found that cesium doping do not change crystalline structure of CdO.
nanocrystals. The average particle size was calculated using Debye-Scherrer’s equation\textsuperscript{162}. The XRD data shows that the particle size is found to be 47 nm for CdO, 44 nm for 3 % Cs doped CdO, and 7 % Cs doped CdO have 41 nm. It shows that the crystalline size of CdO nanoparticles decreases due to presence of cesium dopant. In comparison with pure CdO nanoparticles the cesium encapsulated CdO have relatively small particle size indicating that the doping can improve the morphology and retard the grain growth of CdO nanoparticles.

2.3.4B. SEM and EDAX analysis:

The SEM images along with EDAX of synthesized CdO, 3 %, and 7 % Cs doped CdO samples are presented by Fig. 2.13. The morphology of the CdO nanoparticles is cubic in nature with agglomerates while 3 % and 7 % Cs doped CdO nanoparticles shows rod like structure along with cubic morphology. The average particle size varies in the range of 47 to 41 nm as measured using the XRD patterns. Strong peaks of Cd and O are found in the EDAX spectrum and also definite amount of cesium indicate that cesium ion has doped into CdO nanoparticles. The EDAX spectrum shows that 2.98 % and 6.93 % of cesium ion is present in the Cs doped CdO nanoparticles which indicate the doping of cesium ion into the nanocrystalline CdO material. The slight decrease in the amount of cesium in Cs doped CdO nanoparticles are due to the washing.

2.3.5B. TEM and SAED analysis:

The size and morphological information of the sample was investigated by TEM and SAED analysis and are depicted in Fig. 2.14. The TEM image of CdO nanoparticles shows the cubic structure, while 3 % or 7 % Cs doped CdO nanoparticles shows rod like structure along with cubic morphology. Moreover, the particle size of the synthesized CdO nanoparticles obtained from TEM analysis is
Fig. 2.10: UV-DRS spectra of synthesized CdO, 3 %, and 7 % Cs doped CdO

Fig. 2.11: FT-IR spectra of synthesized CdO, 3 %, and 7 % Cs doped CdO

Fig. 2.12: XRD pattern of synthesized CdO, 3 %, and 7 % Cs doped CdO
Fig. 2.13: SEM and EDAX of a) synthesized CdO, b) 3 % Cs doped CdO, and c) 7 % Cs doped CdO
similar to those estimated from Debye-Scherrer equation\textsuperscript{162} and in the range of 47 to 41 nm. The dark spot in the TEM micrograph can be alluded to the synthesized CdO, 3 %, and 7 % Cs doped CdO nanoparticles as SAED pattern associated with such spots reveals the occurrence of CdO, 3 %, and 7 % Cs doped CdO nanoparticles in total agreement with the XRD data. The SAED pattern of CdO, 3 %, and 7 % Cs doped CdO nanoparticles shows similar d-values as obtained from XRD data.

\textbf{2.3.6B. Thermogravimetric analysis (TGA)}:

Figure 2.15 illustrates the curve of thermogravimetric analysis of the CdO nanoparticles. TGA curve shows the decomposition of CdO nanoparticles is performed in a two step pattern of the weight loss. The first weight loss of 2.743 % is observed in the range of temperature between 279.23-314.84\textdegree C, which can be related to decomposition of adsorbed water molecules. The second weight loss of 1.947 % is observed in the temperature range 314.84-374.90\textdegree C can be associated with decomposition of the organic contents in the precursor. It was found that the weight loss terminates at 400\textdegree C and stable in 400-500\textdegree C, so this temperature was determined as the calcinations temperature of the intermediate molecules and reaching the CdO phase.

\textbf{2.3.7B. Photoluminescence analysis (PL)}:

The photoluminescence spectrum of the CdO nanoparticles shows blue shift in relation to the bulk, and the band gap (bulk CdO, 538 nm) is shown by Fig. 2.16. The emission wavelength of the CdO nanoparticles is at ~563 nm (E= 2.2 eV), dependent on the particles size (quantum size effect) which is the band edge or near band edge emission, and considered due to transition between valence and the conduction bands. The relatively large width of the emission band of the CdO nanoparticles is due to the broad distribution of intra-band states associated with different trapping sites. The
Fig. 2.14: TEM and SAED of a) synthesized CdO, b) 3 % Cs doped CdO, and c) 7 % Cs doped CdO
blue shift in the excitation absorption reflects the correspondingly gradual removal of
the initial trap, and surface states during the crystallization process of nanoparticles.
By controlling the morphology, the optical property of CdO nanostructures can be
tunable which will be useful for the photodegradation applications.

2.3.8B. BET surface area analysis:

The BET surface area measurement curves for synthesized CdO, 3 %, and 7 %
Cs doped CdO nanoparticles are shown in Fig. 2.17. The N₂ adsorption-desorption
isotherms and BJH pore size distribution of CdO nanoparticles reveals that the sample
have typical IV N₂ adsorption-desorption isotherms with H₁ hysteresis. All the
samples have a narrow pore diameter range. Based on the N₂ adsorption-desorption
isotherms the specific surface area (S_{BET}) of CdO nanoparticles is 29.71 m²/g, the
average pore volume (V_p) and pore diameter (dp) were 0.04630 cc/g, and 24.87 Å
respectively. In 3 %, and 7 % Cs doped CdO nanoparticles the specific surface area
(S_{BET}) obtained from BET method is 36.27 m²/g, and 57.13 m²/g, the average pore
volume (V_p), and pore diameter (dp) were 0.04832 cc/g, 0.05769 cc/g, 30.92 Å, and
31.09 Å respectively. The modified (Cs-doped) CdO nanoparticles have large surface
area, average pore volume and pore diameter than pure CdO nanoparticles.
Fig. 2.15: TGA curve of synthesized CdO nanoparticles

Fig. 2.16: PL spectrum of synthesized CdO nanoparticles
Fig. 2.17: BET surface area, and pore size of a) synthesized CdO, b) 3% Cs doped CdO, and c) 7% Cs doped CdO.
Section-C

Synthesis and Characterization of Semiconducting PbS and Co Doped PbS Nanoparticles

2.1C. Introduction:

Nanocrystals of inorganic semiconductors are well suited for the development of novel optoelectronic devices due to their flexibility and simple processability combined with optical properties. Nanocrystals exhibit photoluminescence with high quantum efficiencies and emission as well as the absorption is strongly size tunable due to their strong quantum confinement\(^{201}\). The lead sulphide (PbS) nanoparticles is an IV-VI group semiconductor materials with direct narrow band gap of 0.41 eV at room temperature\(^{202}\), a large excitation Bohr radius of 18 nm\(^{203}\), high dielectric constant (18)\(^{204}\), and very high carrier mobility (0.44 cm\(^2/V/s\))\(^{205}\). There is a broad spectrum of sulphide materials used in semiconductor material science and technology\(^{206}\).

Among the inorganic nanoparticles lead sulphide (PbS) semiconducting nanoparticles have received great attention because of their potential uses as photonic material, and Pb\(^{2+}\) ion selective sensors\(^{207}\). Due to its optical and electronic properties it used in photography\(^{208}\), IR detector\(^{209}\), and solar absorption\(^{210}\). The PbS nanoparticles have non linear optical properties therefore have extensive applications in optical device like optical switch\(^{211}\). A lead sulphide nanomaterial has promising photosensitive properties and act as a good photocatalyst\(^{212}\). Lead sulphide nanoparticles have unique photoconductive properties therefore it is used in mid infrared lasers\(^{213}\), photoresistants, humidity and temperature sensors, decorative and solar control coatings, and diode lasers\(^{214}\). The lead sulphide nanoparticles have
diverse applications including telecommunications\textsuperscript{215}, and microscopic imaging in the biological transparency window\textsuperscript{216}. Oleic acid capped PbS nanoparticles has antiwear, friction-reduction properties, and used as an additive in liquid paraffin\textsuperscript{217}. Lead sulphide detectors have great demand as sensors for military systems, industrial, commercial, and medical applications\textsuperscript{218}. Lead sulphide (PbS) nanoparticles can show multiple exciton generation (MEG) in which the impact of single photon produces two or more excitons\textsuperscript{219}, these phenomenon has raised photo conversion efficiency of the material\textsuperscript{220}.

The size, shape, capping material, and surface characteristics have a strong influence on the optical properties of PbS nanocrystals. The large ratio of surface to volume in semiconductor nanoparticles results in strong influence of the surface states on their optical properties\textsuperscript{221}. Lead sulphide (PbS) nanoparticles have been synthesized by several physico-chemical methods including solvothermal\textsuperscript{222}, electron beam irradiation\textsuperscript{223}, sonochemical\textsuperscript{224}, solid state reaction\textsuperscript{225}, microemulsion\textsuperscript{226}, chemical precipitation\textsuperscript{227}, sol-gel process\textsuperscript{228}, chemical co-deposition\textsuperscript{217} precursor, and dual source method\textsuperscript{229}, chemical method\textsuperscript{230}, chemical bath deposition\textsuperscript{231}, hydrothermal method\textsuperscript{232}, and gas phase synthesis\textsuperscript{233}.

Chalcogenides of cadmium, lead, and zinc have proved their potential as efficient absorbers of electromagnetic radiation\textsuperscript{234}. In order to achieve more efficient lead sulphide (PbS) nanoparticles, they were synthesized by hydrothermal method. The modified nanoparticles have shown high absorption of visible light, and good electron transfer properties\textsuperscript{235}, therefore cobalt doped lead sulphide nanoparticles was also synthesized. The goal of this study is to investigate the effect of cobalt ion doping on the catalytic activity of lead sulphide nanoparticles. The synthesized PbS, and cobalt doped PbS nanoparticles was characterized by using different analytical
techniques like UV-DRS, PL, FT-IR, XRD, SEM, EDAX, TEM, SAED, TGA, ESR, and BET surface area measurements.

2.2C. Experimental:

The starting materials lead nitrate (Sigma Aldrich, 99.0 %), triton X-100 (Qualigens, 99.0 %), sodium sulphide (Loba Chemie, 60.0 %), cobalt nitrate (Loba Chemie, 99.0 %), and sodium hydroxide (Sigma Aldrich, 98.5 %) were used for the synthesis of PbS and Co doped PbS nanoparticles.

2.2.1C. Synthesis of PbS nanoparticles:

A triton X-100 as a capping agent (0.05 mol) was added to a magnetically stirred solution of lead nitrate (1.0 mol) at room temperature. The solution of sodium sulphide (1.0 mol) was added in the reaction mixture and reaction mixture was homogenized by stirring over 20 mins at room temperature. The aqueous solution of sodium hydroxide (1.0 N) was added slowly in above solution and stirred until solution becomes alkaline. The complex formation was obtained as a precipitate and it was stirred for further 2 hrs at room temperature. The white solid product obtained was filtered, washed thoroughly with distilled water for the complete removal of nitrate, hydroxide ion, and to remove the soluble impurities. The precipitate was dried in oven at 120ºC for 2 hrs and ground mechanically to fine powder. The resulting dry powder was calcinized at 500ºC for 4 hrs at the rate of 2ºC per minute.

2.2.2C. Synthesis of Co doped PbS nanoparticles:

The synthesized lead sulphide (PbS) nanoparticles were used as precursor material and cobalt nitrate as dopant. An initially lead sulphide nanoparticle (1.0 mol) was mixed with 5 % and 10 % cobalt nitrate solution along with sodium hydroxide solution (1.0 N, 10 ml). The slurry obtained was stirred well and transferred into teflon autoclave and kept in oven at 110ºC for 20 hrs. The precipitate obtained was
filtered, washed with distilled water for the removal of soluble impurities, and dried at 120°C for 2 hrs. These samples were calcinized at 500°C for 2 hrs. The calcinized 5 %, and 10 % Co doped PbS nanoparticles are used for characterization.

2.3C. Results and Discussion:

2.3.1C. UV-DRS analysis:

The UV-DRS of the nanocrystalline PbS, 5 %, and 10 % Co doped PbS nanoparticles is shown in Fig. 2.18. The spectra show broad band at 295, 298, and 304 nm for PbS, 5 %, and 10 % Co doped PbS nanoparticles respectively. With increase in the amount of dopant the band position shifted to higher wavelength side. From these the band gap energy of the synthesized PbS, 5 %, and 10 % Co doped PbS nanoparticles are 4.20, 4.16, and 4.07 eV respectively. The shifting of band arises due to doping effect on band gap of lead sulphide (PbS) semiconducting nanoparticles. The band gap of PbS nanoparticles can be significantly blue shifted from the near infra red to the near ultraviolet region with decreasing particle size compared to bulk counterpart.

2.3.2C. FT-IR analysis:

The FT-IR spectra for the synthesized PbS, 5 %, and 10 % Co doped PbS nanoparticles in KBr matrix is shown in Fig. 2.19. The absorption band at 3413.31 cm\(^{-1}\) are attributed to the stretching vibration of the OH group due to small amount of water adsorbed on the surface of PbS nanoparticles\(^{160}\). The absorption band at about 1396.57 cm\(^{-1}\) is due to the CH\(_2\) vibration. The absorption band at 480.29, 599.88, 1066.67, and 2033.04 cm\(^{-1}\) showed characteristic frequency of Pb-S bond and bands at around 480.29 and 599.88 cm\(^{-1}\) are broadened due to encapsulation of cobalt ion into the PbS nanoparticles. The band at 1066.67 cm\(^{-1}\) becomes more pronounced in Co
doped PbS nanoparticles, and the broad nature of band increases with increase in amount of cobalt ion.

2.3.3C. X-ray diffraction (XRD) analysis:

Figure 2.20 shows the XRD patterns of synthesized PbS with various Co$^{2+}$ doping. The diffraction peaks indicate the nanocrystalline nature of synthesized materials. It shows peaks at an angle 28.5, 32.7, 48.2, 52.6, 58.7, and 67.4 corresponds to the reflection from 111, 200, 220, 311, 222, and 400 crystal planes respectively. The XRD pattern is in agreement with the cubic structure of lead sulphide sample (JCPDS Card No. 78-1057) with space group Fm3m (225). Sharp diffraction peak indicates good crystallinity of PbS nanoparticles. The XRD pattern of 5 % and 10 % Co doped PbS sample is almost coincide with that of pure PbS also showing no significant diffraction peaks due to encapsulation of cobalt ion. It indicates that cobalt is present in ionic state bonded with sulphur of the PbS inside the frame work.

The average particle size was calculated using Debye-Scherrer’s equation$^{162}$, and particle size obtained for PbS is 31 nm, 5 % Co doped PbS nanoparticles is 29 nm, and 10% Co doped PbS nanoparticles is 26 nm. In comparison with pure PbS nanoparticles the Co encapsulated PbS nanoparticles has relatively small particle size indicating that the doping can improve the morphology, and retard the grain growth of PbS nanoparticles. This may be due to the fact that dopant ion inhibits crystal growth and sintering between grains during the heat treatment Pb$^{+2}$ atoms in crystal lattice is replaced by Co$^{+2}$ ion. Transition metal ion (cobalt) encapsulation enhances the interfacial charge transfer reaction of PbS nanoparticles and decreases the crystallite size of lead sulphide (PbS) nanoparticles.
Fig. 2.18: UV-DRS spectra of synthesized PbS, and (5 %, and 10 %) Co doped PbS

Fig. 2.19: FT-IR spectra of synthesized PbS, and (5 %, and 10 %) Co doped PbS

Fig. 2.20: XRD pattern of synthesized PbS, and (5 %, and 10 %) Co doped PbS
2.3.4C. SEM and EDAX analysis:

The SEM images of synthesized PbS, 5 %, and 10 % Co doped PbS nanoparticles are shown by Fig. 2.21. The SEM image of synthesized PbS nanoparticles shows dumbell shaped morphology. The SEM images of 5 % Co doped PbS nanoparticles shows rod like structure and the SEM image of 10 % Co doped PbS nanoparticles shows agglomerates. However, the size of the particles varies in the range of 31 to 26 nm, which is similar to values obtained by XRD data. The EDAX analysis of synthesized PbS, 5 %, and 10 % Co doped PbS nanoparticles are shown in Fig. 2.21. Strong peak of Pb and S are found in the EDAX spectrum and amount of cobalt indicate that cobalt ion has doped into PbS nanocrystallites. The spectrum indicates that 4.95 %, and 9.98 % of cobalt ion is present in the doped PbS nanoparticles. The slight decrease in the amount of cobalt is due to the leaching of unbound cobalt ion during the washing.

2.3.5C. TEM and SAED analysis:

The size and morphological information of the sample was further investigated by TEM, SAED analysis, and are depicted in Fig. 2.22. The TEM image of PbS, 5 %, and 10 % Co doped PbS nanoparticles shows cubic structure along with agglomerates. Moreover, the particle size of the sample obtained from TEM analysis is comparable to those estimated from Debye-Scherrer equation\textsuperscript{162} and in the range of 31 to 26 nm. The dark spot in the TEM micrograph can be alluded to the synthesized PbS, 5 %, and 10 % Co doped PbS nanoparticles as SAED pattern associated with such spots reveals the occurrence of PbS, 5 %, and 10 % Co doped PbS nanoparticles, and is in total agreement with the XRD data. The SAED pattern of PbS, 5 %, and 10 % Co doped PbS nanoparticles shows similar d-values as obtained by XRD data.
Fig. 2.21: SEM and EDAX of a) synthesized PbS, b) 5% Co doped PbS, and
c) 10% Co doped PbS
2.3.6C. Thermogravimetric analysis (TGA):

Figure 2.23 illustrates the curve for thermogravimetric analysis of the PbS nanoparticles. According to this curve the weight loss of 1.15 % is observed in the range of temperature between 0-450°C, which can be related to decomposition of adsorbed water molecules, and decomposition of the organic contents in the precursor. It was found that the weight loss terminates at 450°C, so this temperature was determined as the calcination temperature of the intermediate molecules, and reaching the PbS phase. The PbS nanoparticles are stable within the 450°C to 650°C temperature region because it shows steady nature.

2.3.7C. Electron spin resonance (ESR) analysis:

Interaction of the cobalt ion, and the host PbS semiconducting nanoparticles studied by ESR spectrum and represented in Fig.2.24. This technique has been used to characterize the environment of the paramagnetic species in host lattice of different species\(^{163}\). The ESR signal of 5 % Co doped PbS nanoparticles was recorded at room temperature. The ESR spectrum indicates that the doping of transition metal (cobalt) is homogeneous, and there is no secondary phase present. The ESR signal also shows that the effective ‘g’ factor is greater than 2 (2.00224) indicates a clear evidence of ferromagnetism in this synthesized materials. This ‘g’ value also used to determine the number of unpaired electrons in the molecule.

2.3.8C. Photoluminescence analysis (PL):

The PL property of PbS nanoparticles is measured at room temperature, and obtained PL spectrum is shown in Fig. 2.25. The emission wavelength of the PbS nanoparticles is at 476 nm (E = 2.60 eV), and 502 nm (E = 2.47 eV), this confirms the quantum size effect, strong confinement compared with bulk PbS, and due to the
Fig. 2.22: TEM and SAED of a) synthesized PbS, b) 5 % Co doped PbS, and c) 10 % Co doped PbS
transitions from the conduction band to interstitial sulphur or lead vacancies and from these vacancies to valence band. However, it should be pointed out that the photoluminescence peak observed in this work is relatively broad indicating in order to achieve semiconductor nanoparticles with a narrow size distribution. The relatively large width of the emission band of the PbS nanoparticles is due to the broad distribution of intra-band states associated with different trapping sites.

2.3.9C. BET surface area analysis:

The BET surface area measurement curve of synthesized PbS, 5 %, and 10 % Co doped PbS nanoparticles is shown by Fig. 2.26. It shows that all the sample have a narrow pore diameter range. Based on the N\textsubscript{2} adsorption-desorption isotherms, the specific surface area (S\textsubscript{BET}) of PbS, 5 %, and 10 % Co doped PbS nanoparticles are 15.65 m\textsuperscript{2}/g, 35.27 m\textsuperscript{2}/g, and 42.80 m\textsuperscript{2}/g. The average pore volumes (V\textsubscript{p}) were 0.02649 cc/g, 0.05631 cc/g and 0.07414 cc/g for PbS, 5 %, and 10 % Co doped PbS nanoparticles. The pore diameter (dp) were 24.80 Å, 32.83 Å, and 38.07 Å for PbS, 5 %, and 10 % Co doped PbS nanoparticles. The surface area, average pore volume, and pore diameter of synthesized Co doped PbS nanoparticles increases with increase in amount of cobalt ions.
Fig. 2.23: TGA curve of synthesized PbS nanoparticles

Fig. 2.24: ESR spectra of PbS, and 5 % Co doped PbS nanoparticles

Fig. 2.25: Photoluminescence spectrum of synthesized PbS nanoparticles
Fig. 2.26: BET surface area, and pore size of a) synthesized PbS, b) 5 % Co doped PbS, and c) 10 % Co doped PbS.
Section-D

Synthesis and Characterization of Semiconducting ZnS and Sm Doped ZnS Nanoparticles

2.1D. Introduction:

The optical properties of II-VI sulphide semiconductor nanomaterial have been studied due to their wide application in electroluminescence devices, light emitting devices, bioimaging technologies, sensors, biological sensors, catalysis, and solar energy cells\textsuperscript{236, 237} because of their unique size dependent electronic, magnetic, optical, and electrochemical properties. Zinc sulphide (ZnS) semiconducting nanoparticles with zinc blende and wurtzite crystal structure having band gap energies of 3.68 and 3.80 eV at room temperature respectively therefore, widely used in electroluminescence, photoluminescence, and cathodoluminescence devices\textsuperscript{238}. The zinc sulphide nanoparticles exhibit size dependent properties such as tuning of band gap with particle size a blue shift of absorption and an enhancement of photocatalytic activities with decreasing crystallite size which arises due to large number of surface atoms, and three dimension confinement of electrons\textsuperscript{239}.

The ZnS nanoparticles also used in photovoltaic devices, transducers optical coating, field effect transistors, flat panel displays, solar cells, and field emission devices\textsuperscript{240}. Luminescent properties of semiconductor nanoparticles have been applied in different field including luminescence tagging, light emitting devices, cellular imaging, immunoassay, and drug delivery\textsuperscript{241}. The semiconducting nanoparticles used in chemical or electrochemical reaction due to its chemiluminescence property which combines chemical reaction with electromagnetic reaction\textsuperscript{242}. The nanoparticles are used as active catalyst for catalyzing the gas phase chemiluminescence\textsuperscript{243}. In zinc
sulphide nanoparticles the photoluminescence phenomenon produced by photoexcitation, electroluminescence, and cathodoluminescence\textsuperscript{244}. The enhanced properties of zinc sulphide nanoparticles used in chemical industry, semiconductor technology, environment protection, and medicine\textsuperscript{245}. The excitonic Bohr radius of zinc sulphide (ZnS) nanoparticles is 2.5 nm\textsuperscript{246}, it is used in small biomolecular probes for fluorescence, and laser scanning microscopy.

The number of surface atom increases as the materials becomes smaller, and its surface energy increases. The increased surface energy and quantum confinement effect have a tremendous effect on the absorption spectra, and photo luminescence property. The metal doped ZnS have very high quantum efficiency with luminescence decay faster than in the bulk crystals, it is used in biolabeling due to its long luminescence life time\textsuperscript{247} and field emission devices\textsuperscript{248}. The doped ion act as recombination centers for the excited electron hole pairs and result in different optical properties therefore have application in photoluminescence, and electroluminescence fields\textsuperscript{249}. The metal doped ZnS nanoparticles are efficient light-emitting material\textsuperscript{250} and exhibit interesting magneto-optical properties\textsuperscript{251}. The metal doped ZnS nanoparticles give the luminescence in various regions as well as improve the properties of ZnS nanoparticles\textsuperscript{252}. The surface modified ZnS nanoparticles have antiwear ability, and used as an additive in liquid paraffin\textsuperscript{253}.

The size, shape, capping material and surface characteristics have a strong influence on the optical properties of the nanocrystals. Zinc sulphide (ZnS) nanoparticles have been synthesized by several physicochemical methods including, hydrothermal\textsuperscript{254}, gamma irradiation\textsuperscript{255}, solvothermal\textsuperscript{256}, microwave\textsuperscript{257}, sono-chemical\textsuperscript{258}, micro-emulsion\textsuperscript{259}, mechano-chemical\textsuperscript{237}, sol-gel method\textsuperscript{246}, reverse
micelle method\textsuperscript{260}, solid state reaction\textsuperscript{261}, solid-liquid chemical reaction\textsuperscript{262}, sputtering\textsuperscript{263}, co-evaporation\textsuperscript{264}, and wet chemical method\textsuperscript{265}.

In order to achieve more efficient zinc sulphide (ZnS) nanoparticles, it was synthesized by hydrothermal method. Samarium doped zinc sulphide (ZnS) nanoparticles were also synthesized to extend the light absorption spectrum of zinc sulphide nanoparticles towards the visible region. The goal of this study is to investigate the effect of samarium ion doping on the catalytic activity of zinc sulphide (ZnS) nanoparticles. The synthesized ZnS and Sm doped ZnS nanoparticles are characterized by analytical techniques like UV-DRS, photoluminescence spectroscopy (PL), FT-IR, XRD, SEM, EDAX, TEM, SAED, TGA, ESR, and BET surface area measurements.

2.2D. Experimental:

All reagents used in experiments are of analytical grade and used without further purification. The starting materials zinc nitrate (Sigma Aldrich, 99.0 %), sodium dodecyl sulphate (Loba Chemie, 99.5 %), sodium sulphide (Loba Chemie, 99.0 %), samarium nitrate (Sigma Aldrich, 99.9 %), and sodium hydroxide (Sigma Aldrich, 98.5 %) were used for the synthesis of ZnS and Sm doped ZnS nanoparticles.

2.2.1D. Synthesis of ZnS nanoparticles:

A sodium dodecyl sulphate as a capping agent (0.02 mol) was added to a magnetically stirred solution of zinc nitrate (1.0 mol) at room temperature. The solution of sodium sulphide (1.0 mol) was drop wise added in the reaction mixture, and reaction mixture was homogenized by stirring over 20 mins at room temperature. The aqueous solution of sodium hydroxide (1.0 N) was added slowly and stirred until solution becomes alkaline. The complex formation was obtained as a precipitate and it was stirred for 5 hrs at room temperature. The white solid precipitate obtained was
filtered, washed thoroughly with distilled water for the complete removal of nitrate, hydroxide ion, and to remove the soluble impurities. The precipitate was dried in oven at 120°C for further 2 hrs and ground mechanically to fine powder. The resulting dry powder was calcinized at 400°C for 2 hrs at the rate of 2°C per mins and the calcinized sample used for characterization.

2.2.2D. Synthesis of Sm doped ZnS nanoparticles:

Above prepared ZnS nanoparticles were used as precursor material and samarium nitrate as dopant. Initially zinc sulphide nanoparticles (1.0 mol) were mixed with 3 % and 7 % samarium nitrate solution along with sodium hydroxide solution (1N, 10 ml). The slurry obtained was stirred well, transferred into teflon autoclave and kept in an oven at 120°C for 20 hrs. The precipitate obtained was vacuum filtered, washed with deionized water for the removal of soluble impurities, and dried at 120°C for 2 hrs. The prepared powders were calcinized at 400°C for 2 hrs. These calcinized 3 % and 7 % Sm doped zinc sulphide are used for characterization.

2.3D. Results and Discussion:

2.3.1D. UV-DRS analysis:

Figure 2.27 shows the room temperature reflectance spectra for ZnS, 3 %, and 7% Sm doped ZnS nanoparticles. The UV-DRS of ZnS, and modified ZnS has absorption edge cut-off at 304, 311, and 318 nm with corresponding band gap 4.07, 3.98, and 3.89 eV respectively. The absorption edge shifted towards the longer wavelength side in Sm doped ZnS nanoparticles. The results obtained shows that after the encapsulation of Sm ion in synthesized ZnS nanoparticles, the absorption goes in the visible region in comparison with undoped ZnS nanoparticles. It means that the doped metal sulphide nanoparticles are sensitive to visible light. The shifting of band is arises due to doping effect on band gaps of ZnS semiconducting nanoparticles and
fundamental absorption corresponds to the transmission from valence band to conduction band. The band gap of ZnS nanoparticles can be significantly blue shifted with increasing the content of Sm ion, and decreasing particle size compared to bulk counterpart. Transition metal ion encapsulation enhances the interfacial charge transfer reaction of zinc sulphide, and decrease the crystallite size of zinc sulphide nanoparticles.

2.3.2D. FT-IR analysis:

IR spectroscopy was used to confirm the formation of the crystalline material. Figure 2.28 represents the FT-IR spectra for the synthesized ZnS, 3 %, and 7 % Sm doped ZnS nanoparticles in KBr matrix. The absorption band at 3421 cm$^{-1}$ is attributed to the stretching vibration of the OH group due to small amount of water adsorbed on the surface of ZnS nanoparticles. The absorption band at about 1627 cm$^{-1}$ is due to the bending vibration of OH group. The absorption band at 420, 960, and 1118 cm$^{-1}$ are associated with Zn-S bond.

2.3.3D. X-ray diffraction (XRD) analysis:

The powder X-ray diffraction patterns of synthesized ZnS, 3 %, and 7 % Sm doped ZnS nanoparticles are shown in Fig. 2.29. The diffraction peaks indicate the nanocrystalline nature of synthesized materials. It shows peak at an angle 12.2, 21.4, 32.3, 33.5, 35.4, and 47.6 corresponds to the reflection from 100, 110, 203, 210, 105, and 215 crystal planes respectively. The XRD pattern is in good agreement with the hexagonal wurtzite structure of zinc sulphide sample (JCPDS Card No. 01-0677) with a space group P6$_3$mc (186), which show obvious size broadening effects, indicating the finite size of the nanoparticles. The XRD pattern of 3 %, and 7 % Sm doped ZnS sample is almost coincide with that of pure ZnS also showing no significant diffraction peaks due to encapsulation of samarium ion. It indicates that samarium is
Fig. 2.27: UV-DRS spectra of synthesized ZnS, and (3 %, and 7 %) Sm doped ZnS

Fig. 2.28: FT-IR spectra of synthesized ZnS, and (3 %, and 7 %) Sm doped ZnS

Fig. 2.29: XRD pattern of synthesized ZnS, and (3 %, and 7 %) Sm doped ZnS
present in ionic state bonded with sulphur of the ZnS inside the framework. The average particle size was calculated using Debye-Scherrer’s equation\textsuperscript{162}.

The particle size of ZnS is 20 nm, 18 nm for 3 % Sm, and 16 nm for 7 % Sm doped ZnS nanoparticles. It clearly reveals that the crystallite size of ZnS decreases in presence of samarium dopant and this method produce the fine particles. In comparison with pure ZnS nanoparticles the Sm encapsulated ZnS nanoparticles have relatively small crystallite size, indicating that the doping can improve the morphology, and retard the grain growth of ZnS nanoparticles. This may be due to the fact that dopant ion inhibits crystal growth, and sintering between grains during heat treatment during the heat treatment Zn\textsuperscript{+2} atoms in crystal lattice is replaced by Sm\textsuperscript{+3} ion. The XRD pattern gives sharper diffraction peaks indicating that it has a better crystallinity of synthesized ZnS and Sm doped ZnS nanoparticles.

2.3.4D. SEM and EDAX analysis:

The SEM images of synthesized ZnS and modified ZnS nanoparticles are shown by Fig. 2.30. The SEM image of synthesized ZnS semiconducting nanoparticles shows hexagonal structure morphology. The SEM image of 3 % and 7 % Sm doped ZnS nanoparticles shows hexagonal morphology and are agglomerates in nature. However, the size of the particles varies in the range of 20 to 16 nm, which is similar to values obtained by X-ray diffraction data. The EDAX analysis of synthesized ZnS, 3 %, and 7 % Sm doped ZnS materials shown by Fig. 2.30. Strong peaks of Zn and S in the EDAX spectrum shows that 2.88 % and 6.84 % of samarium ion is present in the Sm doped ZnS nanoparticles.
Fig. 2.30: SEM and EDAX of a) synthesized ZnS, b) 3% Sm doped ZnS, and c) 7% Sm doped ZnS
2.3.5D. TEM and SAED analysis:

The morphology and structure was investigated by TEM. The image of pure ZnS, and Sm doped ZnS nanoparticles are depicted in Fig. 2.31. The average particle size of pure ZnS and Sm doped ZnS nanoparticles are in between 16 to 20 nm. The results obtained by TEM agree with XRD analysis. The SAED rings mainly indicate the polycrystalline nature of the synthesized ZnS and Sm doped ZnS nanoparticles.

2.3.6D. Thermogravimetric analysis (TGA):

Figure 2.32 illustrates the curve of thermogravimetric analysis of the ZnS nanoparticles. According to this curve, the decomposition of synthesized ZnS performed in a two step pattern. The first weight loss of 3.75 % is observed in the range of temperature between 0-242.34°C, which can be related to decomposition of adsorbed water molecules. The second weight loss of 3.75 % is observed in the temperature range 242.34-280.30°C can be attributed to decomposition of the organic contents in the precursor. It was found that the weight loss terminates at 280.30°C, so this temperature was determined as the calcination temperature of the intermediate molecules. The ZnS nanoparticles are stable within the 280.30°C to 540°C temperature region.

2.3.7D. Electron spin resonance (ESR) analysis:

The ESR technique has been used to characterize the environment of the paramagnetic species. Interaction of the samarium ion the host ZnS semiconducting nanoparticles studied by ESR spectrum, and are shown by Fig. 2.33. The ESR signal of synthesized 3 % Sm doped ZnS nanoparticles were recorded at room temperature. The detail structural characterization indicates that the doping of rare earth metal (samarium) is homogeneous and there is no secondary phase present. The ESR signal also shows that the effective g factor greater than 2 (2.00200) indicates a clear
Fig. 2.31: TEM and SAED of a) synthesized ZnS, b) 3 % Sm doped ZnS, and c) 7 % Sm doped ZnS
Fig. 2.32: TGA curve of synthesized ZnS nanoparticles

Fig. 2.33: ESR spectrum of 3 % Sm doped ZnS nanoparticles

Fig. 2.34: PL spectrum of synthesized ZnS nanoparticles
evidence of ferromagnetism Sm doped ZnS synthesized nanoparticles. This g value also used to determine the number of unpaired electrons in the molecule.

2.3.8D. Photoluminescence analysis (PL):

The photoluminescence spectrum of the ZnS semiconducting nanoparticles is shown in Fig. 2.34. The emission wavelength of the ZnS nanoparticles is at 448 nm (E = 2.76 eV), this confirms the quantum size effect, strong confinement compared with bulk ZnS, arises due to transitions from the conduction band to interstitial sulphur or zinc vacancies, and from these vacancies to valence band. The intensity of emission peak is strong and the emission band is narrow which further indicates the ZnS nanoparticles have a good crystallinity. The relatively large width of the emission band of the ZnS nanoparticles is due to the broad distribution of intra-band states, associated with different trapping sites.

2.3.9D. BET surface area analysis:

The BET surface area measurement spectrum of synthesized ZnS, 3 %, and 7 % Sm doped ZnS nanoparticles are shown by Fig. 2.35. The synthesized Zns and Sm doped ZnS nanoparticles have typical IV N2 adsorption-desorption isotherms with H1 hysteresis. The BJH pore size distribution demonstrates that all the samples have a narrow pore diameter range. Based on the N2 adsorption-desorption isotherms, the specific surface area (S_BET) of ZnS nanoparticles is 36.3 m²/g, the average pore volume (V_P), and pore diameter (dp) were 0.06384 cc/g, and 24.77 Å respectively.

In 3 % Sm doped ZnS nanoparticles, the specific surface area (S_BET) is 41.27 m²/g, the average pore volume (V_P) and pore diameter (dp) were 0.08023 cc/g and 27.81 Å respectively. In 7 % Sm doped ZnS nanoparticles the specific surface area (S_BET) is 48.71 m²/g, the average pore volume (V_P), and pore diameter (dp) were 0.08650 cc/g, and 31.11 Å respectively. The encapsulation of Sm in ZnS
nanoparticles increases the surface area ($S_{BET}$), average pore volume ($V_p$) and pore diameter ($d_p$) of Sm dopd ZnS nanoparticles.
Fig. 2.35: BET surface area, and pore size of a) synthesized ZnS, b) 3 % Sm doped ZnS, and c) 7 % Sm doped ZnS.