Chapter 2

Investigations on structural, optical and magnetic properties of ZnO-CdS composite nanopowder
2.1 Introduction

Semiconductor nanomaterials have been attracted extensive attention due to their size-dependent properties and important potential applications in photovoltaic solar cells, light emitting devices, chemical/biological sensors and photocatalysis [1-4]. Among these materials, ZnO is most suitable semiconductor material for photocatalysts, solar cell applications due to its abundance and environment friendly nature [5]. However, wide bandgap of ZnO (3.37 eV) limits some applications under visible region. The efficiency of ZnO based photocatalysts is supposed to be extremely low. In order to enhance photocatalytic activity, various research groups have proposed visible bandgap semiconductors for effective sensitization, such as CdSe [6], CdTe [7], PbS [8] and CdS [9]. Among these sensitizers, CdS is considered to be most suitable visible sensitizer for ZnO because its bandgap is in visible range; the lattice structure of CdS is same that of ZnO and CdS forms a type-II heterojunction with ZnO which facilitates a very fast inter band charge transfer from CdS to ZnO [10-13]. Moreover the life time of photogenerated charge carriers in ZnO-CdS nanocomposite was observed to be higher than that of pure ZnO and CdS nanostructures [14]. Furthermore, CdS itself is also visible light responsive photocatalyst. Therefore, ZnO-CdS nanocomposites are attracted much attention in the area of photocatalytic solar cell applications [15-17]. Recently, Li et al., reported that ZnO-CdS nanocomposites have good photovoltaic response under visible light irradiation [12]. Zhu et al., reported that short-circuit current density of ZnO/CdS core/shell heterostructures represents a significant improvement over the dye-sensitized solar cells [18].

In the present investigation, ZnO-CdS composite nanopowder was successfully synthesized by chemical precipitation method. The prepared powder was further characterized using different spectroscopic techniques like powder XRD, SEM with EDS analysis, TEM, FT-IR, optical absorption, EPR, PL and VSM.
2.2 Experimental procedure

2.2.1 Materials

The following materials were used as precursors for the synthesis of ZnO-CdS composite nanopowder. Zinc acetate \([\text{Zn(CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O}]\), cadmium acetate \([\text{Cd(CH}_3\text{COO)}_2\cdot 4\text{H}_2\text{O}]\), sodium hydroxide \([\text{NaOH}]\), sodium sulfide \([\text{Na}_2\text{S}]\) and ethanol were used as precursors. Deionized water was used for all dilution and sample preparation. All the chemical reagents used were analytical grade and above 99% in purity without further purification. All the glassware used in this experimental work was acid washed.

2.2.2 Synthesis of ZnO-CdS composite nanopowder

In a typical procedure, 2.2 g (0.2 mol%) of \(\text{Zn(CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O}\) in 50 mL of deionized water-ethanol matrix (equal volumes) and an equal molar amount of sodium hydroxide in another deionized water-ethanol matrix were mixed drop by drop. The mixture was stirred magnetically at 80°C until a homogeneous white solution was obtained. Then, 50 mL deionized water-ethanol matrix of cadmium acetate solution was added to the above solution. After 10 minutes, 50 mL of sodium sulfide solution (prepared in a deionized water-ethanol matrix) was added to the above colloidal solution drop wise with continuous stirring. Subsequently, the white solution turned light yellow, indicating the formation of ZnO-CdS nanocomposite and it is stirred for 4 hours. The obtained dispersions were washed several times with deionized water and ethanol to remove impurities. After washing, the solution was centrifuged at 10,000 rpm about 30 minutes. The settled powder was collected and dried in a hot air oven at 120°C for 2 hours to obtain ZnO-CdS composite nanopowder. The synthesized nanopowder was further characterized by using different spectroscopic techniques.
2.2.3 Characterization

Powder X-ray diffraction was done on PANalytical XPert Pro-diffractometer with Cu Kα radiation (1.5406 Å). SEM and EDS images were taken from ZEISS EVO 18. TEM images are recorded on HITACHI H-7600 and CCD CAMERA system AMTV 600 by dispersing the samples in ethanol. FT-IR spectrum was recorded using KBr pallets on Thermo Nicolet 6700 spectrometer in the range of 4000–400 cm⁻¹. Optical absorption spectrum was taken from JASCO V-670 spectrophotometer in the wavelength region of 200–1400 nm. EPR spectrum was recorded on JEOL JES-TE100 ESR spectrometer operating at X-band frequencies and having 100 kHz field modulation. PL spectrum was obtained from Horiba Jobin-Yvon Fluorolog-3 spectrofluorimeter with Xe continuous (450 W) and pulsed (35 W) lamps as excitation sources. The magnetic hysteresis loop was obtained from a Lake Shore 7407 vibrating sample magnetometer (VSM).
2.3 Results and discussion

2.3.1 Powder X-ray diffraction analysis

X-ray diffraction study is a powerful tool to obtain the information about average crystallite size, micro strain and crystal phase identification. X-ray diffraction pattern of ZnO-CdS composite nanopowder is shown in Fig. 2.1. All the diffraction peaks can be indexed to a mixed phase of hexagonal wurtzite structured ZnO (JCPDS: 36-1451) and CdS (JCPDS: 65-3414). No additional peaks corresponding to any secondary or impurity phase were observed which indicates that impurity ions do not change the structure of host lattice. Broadening of diffraction peaks shows the formation of nanoparticles. X-ray diffraction peaks observed at \(2\theta = 31.68, 34.33, 36.15, 47.46, 56.52, 62.79, 66.36, 67.84, 68.94, 72.49\) and 76.95 are assigned to the diffraction planes (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), (0 0 4) and (2 0 2) of hexagonal wurtzite ZnO with lattice cell parameters \(a = 0.3254\) and \(c = 0.5214\) nm. The peaks observed at \(2\theta = 24.94, 26.38, 27.99, 43.72, 51.82\) are corresponding to the planes (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 1 2) of hexagonal phase of CdS with lattice cell parameters \(a = 0.4136, c = 0.6756\) nm.

![X-ray diffraction pattern of ZnO-CdS composite nanopowder](image)

Fig. 2.1 X-ray diffraction pattern of ZnO-CdS composite nanopowder
The average crystallite size was evaluated using FWHM of maximum intensity peak of ZnO i.e. (1 0 1). The average crystallite size is calculated using Debye-Scherrer’s formula,

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

where \( \lambda \) is wavelength (CuKα), \( \beta \) is full width at half maximum (FWHM), \( \theta \) is diffraction angle. The dislocation density (\( \delta \)) and micro strain (\( \varepsilon \)) were calculated using equations, \( \delta = \frac{1}{D^2} \) and \( \varepsilon = \frac{\beta \cos \theta}{4} \) respectively. The average crystallite size, dislocation density (\( \delta \)) and micro strain (\( \varepsilon \)) are evaluated as 28 nm, \( 1.37 \times 10^{15} \) lines/m\(^2\) and \( 1.26 \times 10^{-3} \) respectively. For crystallite size determination, Scherrer’s equation does not consider lattice strain in the sample. Williamson-Hall (W-H) method is more accurate to estimate the crystallite size and micro strain of prepared powder samples. W-H equation is expressed as

\[ \beta \cos \theta = \left( \frac{0.9 \lambda}{D} \right) + 4 \varepsilon \sin \theta \]

W-H equation represents a straight line between \( 4 \sin \theta \) (X-axis) and \( \beta \cos \theta \) (Y-axis). The slop of the line gives micro strain (\( \varepsilon \)) and intercept (\( k\lambda/D \)) of line represents crystallite size (\( D \)). W-H plot of ZnO-CdS composite nanopowder is shown in Fig. 2.2.

![Fig. 2.2 W-H plot of ZnO-CdS composite nanopowder](image)
Average crystallite size ($D$) and micro strain ($\varepsilon$) are evaluated as 29 nm and $0.43 \times 10^{-3}$ respectively. The crystallite size measured by W-H plots is very close to the values obtained from Debye-Scherrer’s formula.

2.3.2 Morphological studies

SEM is an important technique for the topography study of samples and it gives information regarding the growth mechanism, shape and size of the particles. Fig. 2.3 shows the morphology of ZnO-CdS composite nanopowder at different magnifications. SEM images show the average size of composite nanopowder in the order of nanometer size. From low resolution SEM images, it can be clearly observed that, the prepared nanopowder shows many agglomerates with spherical like morphology. The agglomeration could be induced by densification resulting from the narrow space between particles. The grain sizes observed in SEM micrographs are different from the crystallite size evaluated from powder XRD studies, it is due to segregation among the crystal nucleus [19]. To estimate the chemical compositional details of prepared sample, further performed the EDS analysis. Fig. 2.4 shows the EDS spectrum of ZnO-CdS composite nanopowder. It is clearly indicates the presence of target elements (Zn, O, Cd, S) in the sample.

Fig. 2.3 SEM images of ZnO-CdS composite nanopowder
Fig. 2.4 EDS pattern of ZnO-CdS composite nanopowder

Fig. 2.5 shows the typical TEM micrographs of ZnO-CdS composite nanopowder. TEM images shows spherical like structures with little agglomeration. The particle size is greater than the average size calculated by XRD because of agglomeration of particles during drying process or non-distinguishable interfaces of the crystallites [20].

Fig. 2.5 TEM images of ZnO-CdS composite nanopowder
2.3.3 FT-IR analysis

FT-IR spectrum of ZnO-CdS composite nanopowder is shown in Fig. 2.6. The characteristic bands observed at 515 and 621 cm\(^{-1}\) are attributed to the fundamental vibrational modes of Zn-O [21] and Cd-S [22]. These vibrational modes are indicative of successive synthesis of ZnO-CdS composite nanopowder; this is already conformed by XRD and EDS. The absorption band at 1119 and 1384 cm\(^{-1}\) are assigned to stretching vibrational modes of O-H and C=O respectively. The symmetric bending mode of vibrations of H-O-H is served at 1631 cm\(^{-1}\). The band at 2344 cm\(^{-1}\) represents C-O symmetric bending vibrations of atmospheric CO\(_2\) molecule [23]. The bands observed at 2850 and 2926 cm\(^{-1}\) are attributed to C-H stretching mode of vibrations [24] and the band at 3457 cm\(^{-1}\) is corresponding to O-H stretching vibrations [25].

![FT-IR spectrum of ZnO-CdS composite nanopowder](image)

Fig. 2.6 FT-IR spectrum of ZnO-CdS composite nanopowder
2.3.4 Optical absorption study

Optical absorption spectrum of ZnO-CdS composite nanopowder is shown in Fig. 2.7. The absorption band at 363 nm is due to excitonic absorption which implies to the lower particle size of prepared material [26].

![Absorption Spectrum](image)

Fig. 2.7 optical absorption spectrum of ZnO-CdS composite nanopowder

2.3.5 EPR study

No EPR signal was detected in the spectrum of ZnO-CdS composite nanopowder indicating the absence of paramagnetic impurities.

2.3.6 Photoluminescence study

PL spectrum is very sensitive to the electronic structure of materials. Fig. 2.8 shows room temperature PL spectrum of ZnO-CdS composite nanopowder under the excitation wavelength of 325 nm. It is well known that surface defects play an important role in the luminescence properties of nanostructure. PL spectrum shown four characteristic emission peaks in both UV and visible regions.
Fig. 2.8 PL spectrum of ZnO-CdS composite nanopowder

Hu et al. reported the PL emission of ZnO particles; they observed a strong emission in UV region and a weak one in blue-green region. The strong UV emission at 371 nm for ZnO can be attributed to near band-edge (NBE) emission, coming from the radiative recombination of electrons in conduction band and holes in valance band [27]. Pure CdS shows a broad emission band between 450 and 630 nm which is attributed to surface defects associated with cadmium and sulfur vacancies [28]. In the present investigation, PL spectrum of ZnO-CdS composite nanopowder consists four emission bands at UV and visible regions. The UV emission peaks centered at 367, 380 nm are attributed to NBE emission. The intensity of UV emission peak decreases as compared to pure ZnO; it reveals the enhancement of photocatalytic efficiency of ZnO under visible light, where CdS acts as sensitizer. A sharp blue emission peak at 425 nm can be assigned to surface vacancies like oxygen vacancies and zinc vacancies, i.e. to the recombination of electron-hole pairs at the valance band [29]. A strong green emission peak in the
range of 450-570 nm is blue shifted as compared to pure CdS, which is evidence for electron transfer from CdS to ZnO on excitation.

The CIE 1931 chromaticity diagram of ZnO-CdS composite nanopowder is shown in Fig. 2.9. The calculated chromaticity coordinates of ZnO-CdS composite nanopowder are \((x, y) = (0.1951, 0.4149)\), which indicates the colour vision of prepared sample. The spots on chromaticity diagram represent bluish-green region. Due to colour tenability with excitation wavelength of ZnO-CdS composite nanopowder can be useful for optical display applications [30].
From CIE 1931 chromaticity coordinates \((x, y)\), correlated colour temperature (CCT) is calculated using McCamy equation [31].

\[
\text{CCT} = -449 \, n^3 + 3525 \, n^2 - 6823.3 \, n + 5520.33
\]

where \(n = (x-x_e)/(y-y_e)\) is inverse slope line with \(x_e = 0.3320, y_e = 0.1858\). CCT is an indication of colour appearance of light emitted by the light source. In the present study, CCT is evaluated as 10952 K, which represents orange light emission.

2.3.7 Magnetic study

The magnetization versus magnetic field \((M-H)\) curve measured at room temperature for ZnO-CdS composite nanopowder was carried out by VSM. Fig. 2.10 illustrates the room temperature ferromagnetism of ZnO-CdS composite nanopowder.

![M-H hysteresis loop of ZnO-CdS composite nanopowder](image_url)

**Fig. 2.10** M-H hysteresis loop of ZnO-CdS composite nanopowder
The sample exhibit well-defined hysteresis loops, which is indicative of room temperature ferromagnetic behavior. The small coercivity and small area under the hysteresis loop characterize these materials as soft ferromagnetism. XRD results clearly indicate the absence of impurity phase in the sample therefore the observed ferromagnetism at room temperature is an intrinsic property [32]. The saturation magnetization (Ms), coercive field (Hc) and remnant magnetization (Mr) of the prepared sample were found to be $13.35 \times 10^{-3}$ emu/g, 119.32 Oe and $1.52 \times 10^{-3}$ emu/g. In the present investigation the room temperature ferromagnetism has been observed without any impurity phase indicating a clear improvement in the preparation of ZnO-CdS composite nanopowder. This is possible due to small crystallite size of the materials and by adopting suitable synthesis conditions in the preparation method. Generally, bulk ZnO and CdS are non-magnetic materials. The presence of magnetism in ZnO-CdS composite nanopowder is a size and structure induced change in spin distribution, within the distorted bands structure. This is a dramatic example of new physical properties being induced from nanoscale anisotropic shape and structure. Many groups have reported that the ferromagnetism in oxides is due to the defects such as zinc vacancy, oxygen vacancy, zinc interstitial and oxygen interstitials [33]. Recently Wang et al. [34] reported that Zn vacancy is responsible for ferromagnetism in ZnO thin films and nanowires. But recently, some theoretical group has reported that ferromagnetism in ZnO is due to Zn vacancies and suggested that the origin of magnetism does not result from Zn 3d electron but it is originated from the unpaired 2p electron of O atom in the immediate vicinity of Zn vacancies [35]. Therefore, the room temperature ferromagnetism (RTFM) in ZnO-CdS is due to the Zn vacancies induced spin polarization.
2.4 Conclusion

ZnO-CdS composite nanopowder was successfully synthesized using chemical precipitation method and the following conclusions are drawn

- XRD pattern of the prepared samples exhibited hexagonal phase of ZnO as well as hexagonal phase of CdS. The average crystallite size is found to be 29 nm. The evaluated lattice cell parameters are $a = 0.3254$, $c = 0.5214$ nm for ZnO and $a = 0.4136$, $c = 0.6756$ nm for CdS.

- The morphology of the prepared sample shows non-uniformly distributed spherical like structures. TEM images clearly show spherical like particles with average diameter of 20 nm. EDS analysis confirms the presence of constituent elements of Zn, Cd, O and S.

- FT-IR spectrum showed the characteristic vibrational modes of Zn-O and Cd-S.

- From optical absorption study, the presence of an excitonic absorption band indicates the reduced particle size of the prepared composite nanopowder.

- PL spectrum illustrate the quenching of UV emission with enhanced visible emission for ZnO-CdS composite nanopowder. CIE chromaticity coordinates are evaluated using PL data as $(x = 0.1951, y = 0.4149)$ which shows bluish-green emission. The synthesized composite nanopowder may use in visible light emitting devices and development of solar cell applications.

- Hysteresis of the prepared nanopowder shows intrinsic ferromagnetism at room temperature.
2.5 References


