

# Synthesis of mix Zinc oxide and Cadmium sulphide Nanoparticles, Optoelectronic and antimicrobial activity and application in Water Treatment

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**Abstract:** In the present study we report the synthesis of mix Zinc oxide and Cadmium sulphide nanoparticles by a chemical route. The obtained nanoparticles were characterized by X-ray diffraction (XRD) and UV-VIS absorption. The studies confirmed the nanometer size particles formation within the polymer matrix. A UV-VIS optical spectroscopy study was carried out to determine the band gap of the nanocrystalline mix Zinc oxide and Cadmium sulphide thin film and it showed a blue shift with respect to the bulk value. The synthesized nanoparticles showed interesting optoelectronic properties and tremendous antibacterial activity and can be used for water purification.

**Key words:** Nanoparticle, XRD, UV-VIS absorption, antibacterial

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## I. Introduction

Zinc oxide and Cadmium sulphide nanoparticles have received much attention for their implications in water treatment and optoelectronic properties. ZnO is technologically an important material due to its wide range of optical and electrical properties; also it is a semiconductor crystal with a large binding energy (60 meV) and wide band gap (3.3 eV at 300 K). ZnO nanoparticles are used in a variety of applications such as UV absorption, antibacterial treatment [1], UV light emitters [2], photocatalyst [3] and as an additive in many industrial products. It is also used in the fabrication of solar cells [4], gas sensors [5], luminescent materials [6], transparent conductor, heat mirrors and coatings. Inorganic Nanoparticles are important materials for applications in medicine, such as biosensing, cell imaging, drug delivery, cancer therapy etc [7-8]. According to the Project on Emerging Nanotechnologies (PEN), Zn occupies fifth rank among the most prevalent nanomaterials in consumer products [4].

In developing countries 80% of the diseases are due to bacterial contamination of drinking water. The removal or inactivation of pathogenic microorganisms is most important in wastewater treatment [8]. According to the World Health Organization [7] any water intended for drinking should contain fecal and total coliform counts of 0, in any 100 mL sample. Another serious issue in water resources planning is the protection of water treatment systems against potential chemical and biological terrorist acts [8-9].

Conventional waste water treatment technologies and the methods for disinfection of drinking water like chlorination, ozonation, UV treatment etc demand high capital investment and operation & maintenance cost, and large area. Application of nanotechnology which results in improved water treatment options might help us in removing the finest contaminants from water and with induced specificity to a certain pollutant that destroy or immobilize toxic compounds and pathogens. Heterogeneous photocatalysis is currently being considered as a promising technique for water purification in comparison to other conventional methods [10-11]. Nanomaterials have been gaining increasing interest in the area of environmental remediation mainly due to their enhanced surface and also other specific changes in their physical, chemical and biological properties that develop due to size effects. Nanotechnology offers a lot of promise in the area of water purification owing to large surface to volume ratios offered by nanostructures [12] and the possibility of preparing photocatalytic membranes by growing semiconducting nanostructures on conventional membranes [13-14]. Research is underway to use advanced nanotechnology for purification of drinking water.

## II. Materials and methods

### 2.1 Synthesis of nanoparticles

All the chemicals were of analytical grade and deionized water was used as a solvent. Different sized ZnO and CdS nanoparticles were prepared by chemical co-precipitation method at room temperature [15]. ZnO nanoparticles were prepared with different molar concentrations using zinc sulphate ( $ZnSO_4 \cdot 5H_2O$ ), and CdS quantum dots were synthesized by an ion exchange reaction. The detailed preparation procedure is as follows. 5 wt% solution of PVA,

$\text{CdCl}_2$  and  $\text{ZnSO}_4$  was mixed with various concentrations (1, 2, 3, 4 wt%) under a high stirring rate (200 rpm) condition. The constant temperature  $70^\circ\text{C}$  for 3 h was maintained during the process of stirring. The sample under preparation was kept for 12 h for complete dissolution to get a transparent solution. To this solution, 2 wt%  $\text{Na}_2\text{S}$  was added until the whole solution turns into yellow color and concentrated nitric acid was added to the solution to change the pH of the whole solution. For synthesis, the Zinc sulphate and sodium sulphide were taken in different molar concentration. The obtained precipitate was then filtered washed and dried at room temperature. After drying, the precipitate was crushed to fine powder with the help of mortar and pestle. The size of the quantum dots formed depends on the number of cadmium ions and Zinc ion exchanged.

## 2.2 Test for change in conductivity of water

The conductivity of water was tested for three water samples – distilled water, tap water and sewage water using soil and water analyzing kit.

## 2.3 Test for antibacterial activity

### 2.3.1 Test microorganisms:

*Escherichia coli* (MTCC 739), *Klebsiella pneumonia* (MTCC 432), *Staphylococcus aureus* (MTCC 96) and *Bacillus subtilis* (MTCC 441) were used for antibacterial screening. The microbial cultures were purchased from the “Microbial Type Culture Collection and Gene Bank” (MTCC), Chandigarh, India. The bacterial cultures were maintained on nutrient agar slants and were stored at  $-4^\circ\text{C}$ .

### 2.3.2 Antibacterial assay

Antibacterial assay of mix ZnO and CdS nanoparticles were studied by Well Diffusion Method [16]. The nutrient agar plates were inoculated with 2.0 ml of inoculum by spreading the swab over the plate. With the help of sterile borer, wells of 8mm diameter were cut on the agar plates and loaded with mix ZnO and CdS nanoparticle solution and a standard antibiotic (Tetracyclin). All plates were incubated at  $37^\circ\text{C}$  for 24 hrs. After incubation period, the inhibition diameters were measured with Hi-Media scale. The experiments were performed in triplicate [17-18].

## 2.4 Data analysis

The experiments were conducted in a completely randomized design and repeated three times. The data were analyzed using origin graphic software and SPSS software version-16.

## III. Results

### 3.1 Characterization of mix Zinc oxide and Cadmium sulphide nanoparticles using UV-Vis Spectra analysis

UV-Visible absorption spectroscopy is very efficient technique to monitor the optical properties of nano sized particles. The optical absorption spectra of the nanocrystals were measured using UV-Vis spectrophotometer (Systronics 119) and the absorption spectra was recorded at room temperature over the range 300nm to 800 nm. The band gap energy were determined from the optical absorption spectra. The observed blue shift in the absorption edge is indication of band gap increase owing to quantum confinement effect. The sample A represent the ratio of ZnO: CdS at 2:5 and B represents 3:5.

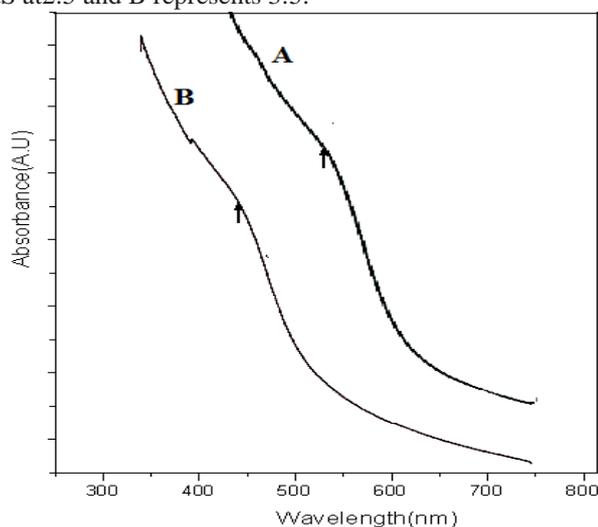


Fig 1. Optical absorption of mix Zinc oxide and Cadmium sulphide

The optical absorption of sample A and B are shown in Fig1. It is evident from the fig1 that sample exhibit a strong absorption at wave length 480nm for B and , 420nm for A suggesting blue shift. The band gap of bulk hexagonal (w) type mix ZnO and CdS is 3.56 and 3.58 eV at 300K. The band gap-energy of the samples are calculated from the optical absorption experiment. From the absorbance(A) and film thickness(t), the absorption coefficient  $\alpha$  ( $\text{cm}^{-1}$ ) is calculated using the equation (1).

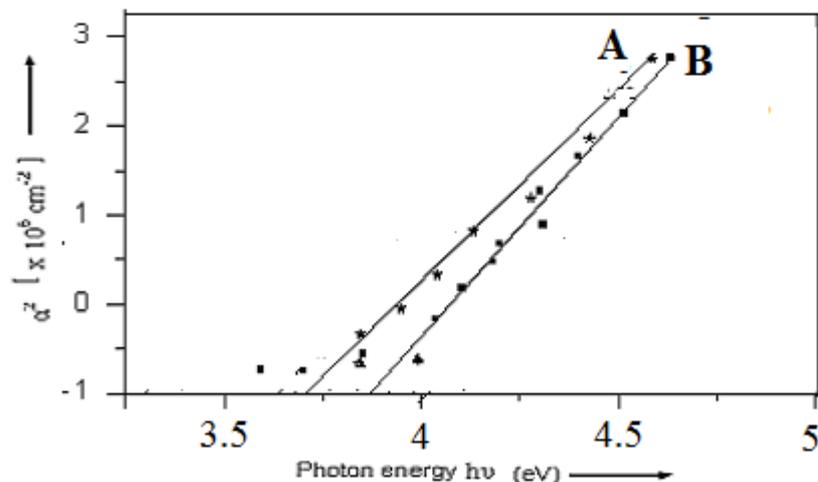


Fig 2 Plot of  $(\alpha h\nu)^2$  versus  $h\nu$  of mix ZnO and CdS nanocomposite for different mixing ratio.

$$\alpha = 2.3026(A/t) \text{-----(1)}$$

The band gap energy of the film at wavelength range 300 to 800nm has been calculated using the equation (3)

$$\alpha^2 = C(h\nu - E_g) \text{-----(2)}$$

Where C is a constant related to the effective masses associated with the bands,  $h\nu$  is the photon energy and  $E_g$  the band gap energy. The band gap energy is measured by a graph of  $\alpha^2$  versus  $h\nu$  data resulting from absorption spectra. The extrapolation fig2 of the straight line to  $\alpha^2=0$  give the value of band gap energy. With the help of hyperbolic band model (HBM) as proposed [18] has been used to explain the change of energy gap as a function of particle size. The equation derived for radius of particle is given

$$E_{gn} = [E_{gb}^2 + 2\hbar^2 E_{gb}(\pi/R)^2 / m^*]^{1/2} \text{--(3)}$$

Where  $m^*$  is the effective mass of the specimen,  $E_{gb}$  is bulk band gap of average value of ZnO and CdS and  $E_{gn}$  is the calculated band gap energy. The corresponding particle size is 7nm for A , 5.5 nm for B, which is in good agreement determined by XRD and HRTEM observation. It is observed that with increase of mixing ratio of CdS and ZnO the band gap increases and particle size decreases.

### 3.2 X-ray diffractions analysis

The XRD patterns of prepared sample were taken by Seifert XRD (3003TT) operating at 40KV-30mA. The radiation source used was  $\text{CuK}\alpha$  ( $\lambda = 1.542\text{\AA}$ ) and a Nickel filter was used to block  $\text{K}\beta$  Radiations. Fig3 represent two different spectra of mix Zinc oxide and Cadmium sulphide nanoparticles with variation mixing ratio. The XRD pattern of A contain broad peaks at  $2\theta = 28.6$  indicating the formation of nanostructure at the ratio of ZnO: CdS at 2:5 and B shows broad peaks at  $2\theta = 31.06$  at the ratio of ZnO: CdS at 3:5

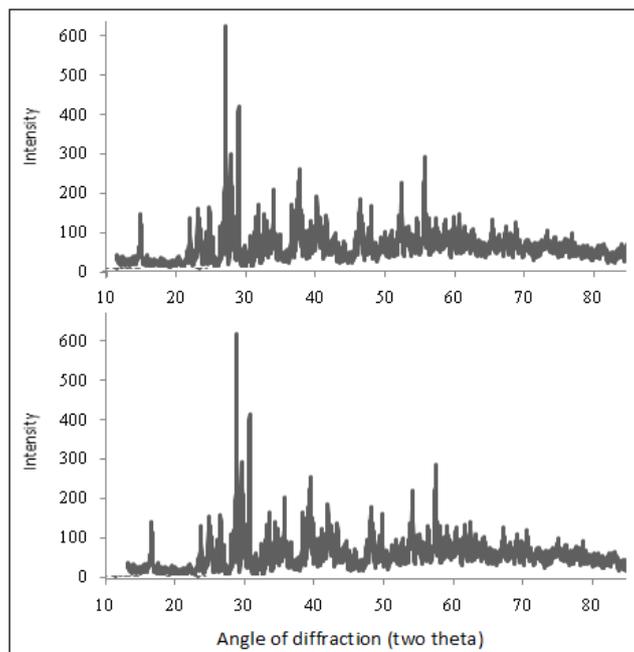


Fig 3. XRD pattern of mix at the ratio of ZnO: CdS at 2:5 and 3:5

The XRD spectrum of both A and B apparently exhibit weak and broad peaks, suggesting small crystallite sizes of hexagonal phase (JCPDS 89-0440). Again it is seen that when the mixing ratio attains equal peaks are more broadened and shifted to higher diffraction angle with decreasing crystal size. The increase in diffraction angle is clearly a result of lattice contraction expected to occur because of higher surface to volume ratio [4]. Some separate peaks are also observed which may be due to CdO because XRD patterns were recorded in ambient condition. The change of phase from hexagonal wurtzite to cubic is observed in nanocrystallite as compared to their bulk counterpart. The grain size of the crystallite are estimated by Scherrer formula [4]

$$D_{hkl} = K \lambda / w \cos\theta \text{----- (4)}$$

w being FWHM &  $\theta$  is the Bragg's angle and  $K=0.89$  for spherical shape (from HRTEM). For calculation  $w$  is observed by zooming the peak position using origin graphics software. The calculated size is found between 4-7 nm.

### 3.3 TEM Observation

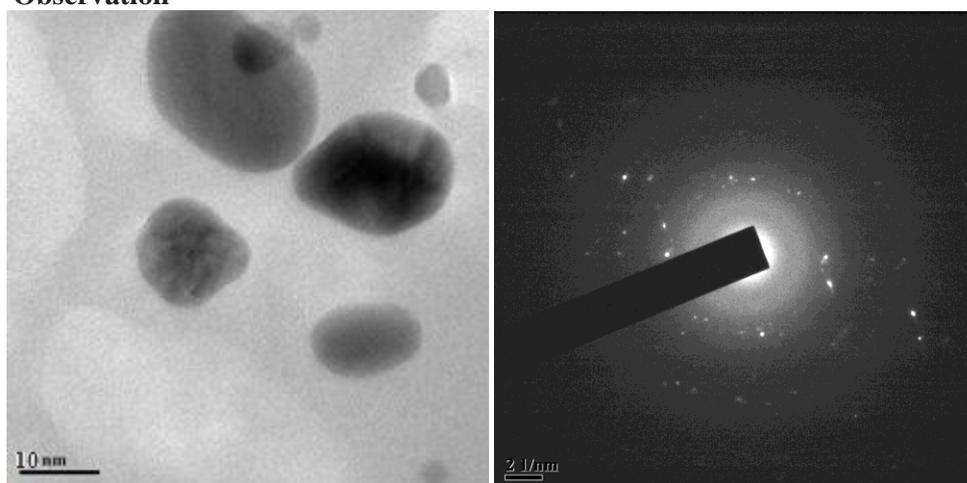


Fig 5. HRTEM image of mix Zinc oxide and Cadmium sulphide nanoparticles.

For direct imaging of nanoparticle and their actual distribution, HRTEM observations were taken at a very high magnification. Prior to HRTEM observation polymer-capped mix ZnO and CdS films were deposited on carbon-coated Cu grids. Figure 5 shows HRTEM micrographs of PVA-capped nanocrystalline mix ZnO and CdS thin films. The micrograph shows the formation of nearly spherical crystallites having diameter in the range of 7-8 nm for different mixing ratio. The average particle sizes obtained from HRTEM observations were found to be nearly similar as those obtained from XRD and HBM model.

### 3.4 Change in Conductivity of water after adding ZnS nanoparticles

Change in conductivity of three different water samples were shown in the table-1. There is an increase in conductivity of water was observed after adding nanoparteciles.

**Table1: change in conductivity of water samples before and after adding ZnS nanoparticles**

Water sample	Change in conductivity	
	Before adding ZnO and CdS nanoparticles	After adding ZnO and CdS nanoparticles
Distilled water	13.34 $\mu\text{s/cm}$	2.08 ms/cm
Tap water	0.716 ms/cm	2.69 ms/cm
Sewage water	0.415 ms/cm	2.23 ms/cm

### 3.5 Antibacterial Activity

Antibacterial activity of the synthesized mix Zinc oxide and Cadmium sulphide nanoparticles was studied for four pathogenic bacteria species. The antibacterial activity was determined *in-vitro* by measuring zone of inhibition in mm using samples at different concentration. Tetracyclin of 1mg/ml, concentration was used as a control antibacterial agent. The results shown in the Table-2 depict that mix Zinc oxide and Cadmium sulphide nanoparticles are efficiently giving zone of inhibition.

**Table 2: Antibacterial efficacy of ZnS nanoparteciles and standard antibiotic against four bacterial strains**

Bacterial Strains	Zone of inhibition of mix ZnO and CdS nanoparteciles (mm)			Tetracyclin (1mgml <sup>-1</sup> )
	50 $\mu\text{g/L}$	80 $\mu\text{g/L}$	100 $\mu\text{g/L}$	
<i>E. coli</i>	18 $\pm$ 0.14	20 $\pm$ 0.11	24 $\pm$ 0.13	35 $\pm$ 0.08
<i>K. pneumonia</i>	19 $\pm$ 0.11	21 $\pm$ 0.16	26 $\pm$ 0.15	32 $\pm$ 0.09
<i>B. subtilis</i>	13 $\pm$ 0.15	18 $\pm$ 0.14	27 $\pm$ 0.11	31 $\pm$ 0.09
<i>S. aureus</i>	16 $\pm$ 0.11	22 $\pm$ 0.08	29 $\pm$ 0.11	34 $\pm$ 0.11

## IV. Discussion

Our study was focused on chemical route synthesis of ZnO and CdS nanoparteciles. The results from UV-Vis spectroscopy and XRD analysis confirms the synthesis of nano sized mix ZnO and CdS which was then used for water conductivity testing and antibacterial assay. The mix ZnO and CdS nanoparteciles are potent in increasing the conductivity of water. We also performed antibacterial assay using disc-diffusion assay. The zone of inhibitions indicates that mix ZnO and CdS nanoparteciles have potentiality for killing water borne pathogenic bacteria.

## V. Conclusion

The mix ZnO and CdS nanoparticles were synthesized successfully through chemical route and their structural as well as optical properties were investigated by using UV-Vis spectrophotometer and XRD. The UV-Visible spectra show a large blue shift attributing the enhanced optical properties changes. We also tested for change in conductivity of water after adding mix ZnO and CdS nanoparteciles. In case of all the three water samples, we observed an increase in conductivity. The mix ZnO and CdS nanoparteciles also showed tremendous antibacterial activity against the water borne pathogens we tested and may be used for water purification. Again mixing ratio takes an important role in outcome result.

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