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## Photocatalytic Activity of Pure and Nickel Doped Cadmium Sulphide Nanoparticles Synthesized via Co-Precipitation Method

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### ABSTRACT

Cadmium sulfide is an important group of II-VI semiconducting nanomaterials with excellent physical properties and wide bandgap energy, are successful in the utilization of photocatalytic application. Photo technology is one of important technology to solve environmental and energy issues. Incorporating a transition metal ion dopant into CdS nanocrystalline is a convenient way to tailor its physical properties. In this present work, we have synthesized transition metal ion - nickel doped CdS nanocrystals via co-precipitation method. The objective of this research is to investigate the photocatalytic activity of pure and nickel doped CdS nanocrystals for the degradation of methylene blue and to provide an experimental base for further study and practical application in textile effluent and wastewater treatment processes. Many factors can influence the performance of photocatalytic activity such as phase composition, crystallite size, morphology, and energy gap. The structural and optical properties of as-synthesized materials were studied by XRD, EDAX, SEM, UV, PL, and FTIR. Photocatalytic degradation of methylene blue was performed by using nickel doped CdS nanoparticles in a photoreactor vessel irradiated by visible light from the tungsten lamp ( $\lambda_{\text{max}}=400 \text{ nm}$ ).

### 1. Introduction

The art of color application to enhance our self-appearance and the world around us has been known to man since time immemorial. The use of natural dyes extracted from vegetables, fruits, plants, flowers, certain insects and fish dating back to 3500 BC have been found. Color is the main attraction of any fabric [1]. The discovery of synthetic dyes by W.H. Perkins in 1856 has provided a wide range of dyes that are colorfast and come in a wider color range and brighter shades [2]. As a result, “dye application” has become a massive industry today. The textile dyeing and finishing industry have created a huge pollution problem as it is one of the most chemically intensive industries on earth, and the No. 1 polluter of clean water. When this effluent is allowed to flow in the fields and rivers it clogs the pores of the soil resulting in loss of soil productivity and quality of drinking water in hand pumps making it unfit for human consumption. It is important to remove these pollutants from the waste waters before their final disposal. Since the significant amounts of dyes are present in the effluent stream in the soluble form, suitable and efficient techniques are highly essential for the treatment of these industrial effluents. In recent years, the visible light induced photodegradation of dyes using nanoparticles is drawing more research interest to make the process more effective, green, and economical. Most of these researches are focused on enhancing the photocatalytic efficiency, by using different doped nanoparticles. In general, for the degradation of the organic dyes, the utilization of electron-hole pairs are playing an important role, on the other hand, the photocatalytic activity is suppressed due to the recombination of electron-hole pair. The best path to enhance the photocatalytic activity is by doping the CdS semiconductor with the transition metals, having magnetic property, such as Fe, Co and Ni [3]. Because, when doping the magnetic transition metal ion like nickel to the host lattice, new defect locations are generated that act as an electron pond and restrains the photogenerated hole-electrons pair recombination. In consequence, created electrons and holes are shifted towards catalyst surface where they contribute to degrading process with the organic pigment.

The objective of this study was to develop an efficient pathway for the degradation of Methylene blue, by doping nickel on CdS, by the chemical precipitation method which is a most viable route and the synthesized photocatalysts were introduced for the degradation of methylene blue dye (MBD) in visible light irradiation. The photocatalytic efficiency of the undoped and nickel doped CdS is compared.

### 2. Experimental Methods

#### 2.1 Preparation of Pure and Nickel Doped CdS Nanoparticle

Samples of pure and CdS nanoparticles were produced by simple chemical precipitation method using analytical grade cadmium acetate, nickel acetate tetrahydrate, and sodium sulfide without purification. A separate solution of 0.2 M of cadmium acetate dihydrate ( $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ ) and nickel acetate tetrahydrate ( $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ ) or were prepared with deionized water. The obtained solution was continuously stirred for 1 hour after that 80 °C heat was supplied to initiate the reaction. 0.2 M of sodium sulfide ( $\text{Na}_2\text{S}$ ) solution was also prepared with deionized water. The prepared 0.2 M of  $\text{Na}_2\text{S}$  was slowly added to the solution and the resultant solution was continuously stirred for another 1 hour and green color precipitate was obtained. The precipitate was further washed with distilled water several times to remove the organic residues present. The obtained nanoprecipitate was allowed to evaporate at room temperature to obtain nickel doped CdS nanoparticles in green color powder form. Similarly, the preparation of undoped orange colored cadmium sulfide Nano powder is also obtained. The residues were tested using the number of methods like XRD, UV, PL, FTIR, EDAX, and SEM.

### 3. Results and Discussion

#### 3.1 Structural Studies

Fig. 1 shows the XRD pattern of the as-synthesized undoped CdS, nickel doped CdS nanoparticles. The X-ray diffraction patterns of undoped CdS and nickel doped CdS catalysts, are found at  $2\theta$  values of 26°, 43° and 52° approximately, referring to diffraction from (111), (220) and (311) planes, respectively [4,5]. The new diffraction peaks may be corresponding to nickel. The XRD patterns obtained for both single CdS and nickel doped

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CdS corresponds to zinc blende or cubic CdS and are consistent with the standard reference JCPDS-89-0440. All the peaks in the diffraction pattern are found to be characteristic of CdS, suggesting that the incorporation of nickel in the sample does not introduce appreciable change in the crystal structure of CdS. The broadening of the diffraction peak provides information about the quantum confinement of the samples. Peak shift can be caused by strain or by changes in chemical composition. The peak shifts occur because of the difference in size of the atoms and repeat distances in the crystal structure to expand or contract depending on whether the doped atom is larger or smaller than the host atom. The crystallite size was calculated using Debye Scherrer's formula,  $D = 0.9\lambda / \beta \cos\theta$ , where  $\lambda$  is the wavelength of X-ray diffraction,  $\beta$  is the FWHM in radians of the XRD peak and the  $\theta$  is the angle of diffraction. The particle size of the sample of three different concentrations is tabulated in Table 1 where D is the diameter of the particles;  $k = 1.518 \text{ \AA}$  (CuK $\alpha$  radiation wavelength). By substituting these values, the size of the undoped cadmium sulfide nanoparticles is 6.93 nm and the size of the nickel-doped nanoparticles is found to be 9.38 nm.

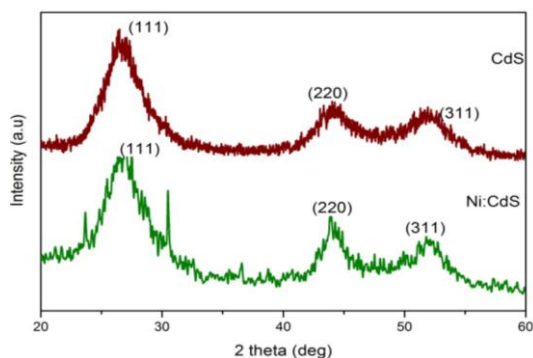


Fig. 1 XRD pattern of pure CdS and nickel doped CdS nanoparticles

Table 1 XRD data of pure CdS, nickel doped CdS

Sample	2 $\theta$ of the intense peak (deg)	FWHM	D spacing	hkl	Average crystallite size (nm)
Undoped CdS	27	1.38	3.2	111	6.93
	45.3	0.9	1.0	220	
	51.9	2	2.75	311	
Nickel doped CdS	26.76	0.98	3.33	111	9.38
	43.67	1.18	2.07	320	
	52.08	0.78	1.75	311	

### 3.2 Optical Properties

The optical properties of quantum-sized particles are observed by UV visible spectroscopy. The absorption spectrum of the undoped CdS and nickel doped CdS nanoparticles is shown in Fig. 2. The spectrums exhibit a well-defined absorption peak at  $\sim 470$  nm, which is considerably blue-shifted relative to the peak absorption of bulk CdS, this blue shift of absorption edge compared to their bulk counterparts clearly explains the quantum confinement effect [6,7], which is due to the presence of dopants incorporated into the nanoparticles of the nickel ions doped into the host materials.

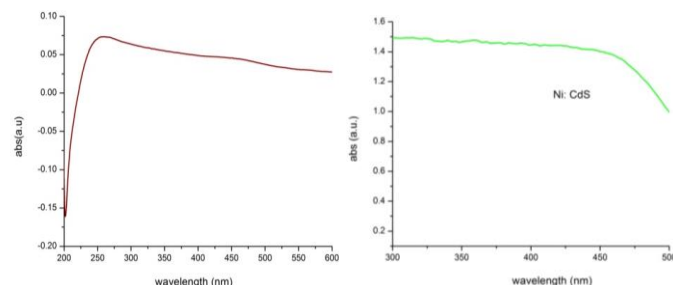


Fig. 2 UV-Vis spectra of CdS and doped CdS

The bandgap of the system is calculated by the equation,  $(\alpha h\nu)^{n/2} = B(h\nu - E_g)$ , where  $\alpha$  is the absorption coefficient,  $\beta$  is a constant called the band tailing parameter,  $h\nu$  is the incident photon energy,  $n$  is an integer. By extrapolating the straight part of this relation to the  $h\nu$  axis, Tauc plot is shown in Fig. 3,  $E_g$  for the nanoparticles. The  $E_g$  calculated for undoped CdS nanoparticle is 2.84 eV, and for the nickel-doped CdS,  $E_g = 2.37$  eV, which are higher than the bulk CdS (2.42eV) (Table 2) due to quantum confinement effect.

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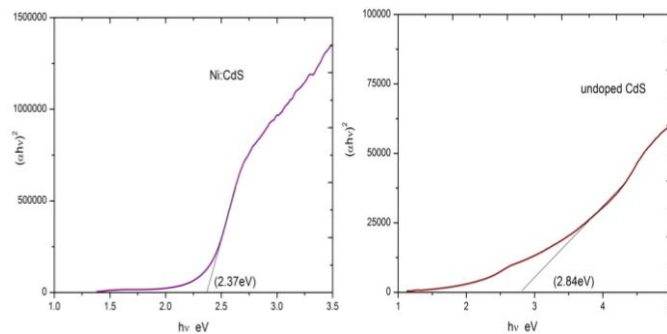


Fig. 3 Tauc plot of doped and undoped CdS

Table 2 Band gap values of nickel ion-doped CdS catalysts from UV-Vis absorbance spectroscopy

Catalysis	Band gap values $E_g$ eV
Undoped CdS	2.84
Nickel doped CdS	2.37

### 3.3 PL Studies

The first strong emission peak at 387 nm can be assigned to the electron-hole recombination of CdS [8] while the other emission peak at 541 nm may be corresponding to the surface trap induced emission.

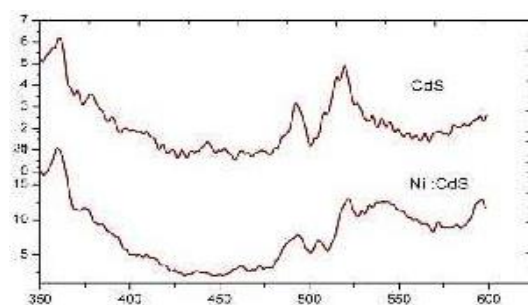


Fig. 4 PL spectra of doped and undoped CdS nanoparticles

Both peaks exhibit a small shift with dopant concentration. This variation in peak energy may be attributed to surface defects. In the case of nickel dopant, not much change in the PL peaks position is observed compared with that of pure CdS (Fig. 4). In doped nanoparticles a large number of dopant centers are concentrated near the surface of the nanoparticles, giving better emission efficiencies compared to that of pure CdS. The ion radii of Cd<sup>2+</sup>, and Ni<sup>2+</sup> is 0.069 nm, and 0.0645 nm, respectively [9,10]. As the dopant radius is small, they can easily incorporate into the sites of the host CdS lattice. The interstitial entrance of dopants of host lattice and hence particle size increases.

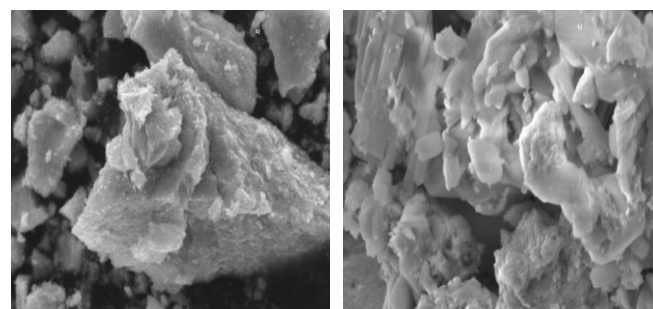


Fig. 5 Pure CdS and nickel doped CdS

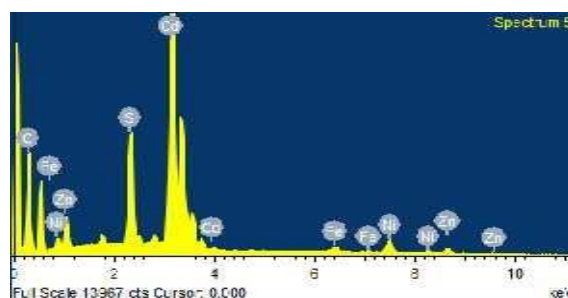


Fig. 6 EDAX of pure CdS and nickel doped CdS

### 3.4 Morphological Study

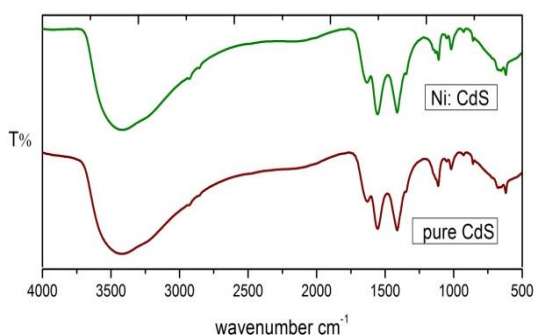
The SEM image of the undoped CdS and Nickel doped CdS nanoparticles is shown in Fig. 5. It is seen that the particles are in nano flakes structure. The successful doping of Ni<sup>2+</sup> into the host (CdS) can be proved by energy dispersive X-ray spectrum which is shown in the Fig. 6 and their atomic percentage ration is tabulated in Table 3.

**Table 3** Composition of Elements in EDAX

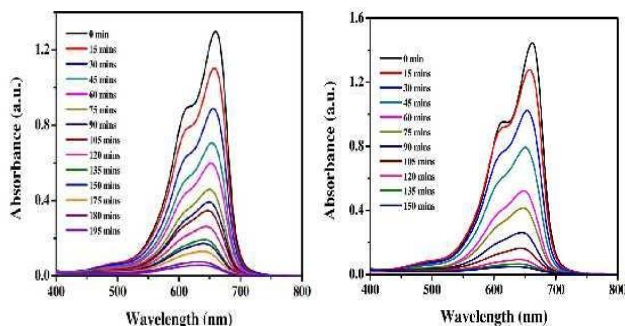
Element	Wt %	At.wt %
C K	19.5	54.86
Ni K	6.56	13.69
Fe L	0.59	0.034
Cd K	12.68	13.19
S K	13.19	17.93

### 3.5 FTIR Study

The FTIR spectra for grown samples CdS and nickel doped CdS were recorded at room temperature as shown in Fig. 7. It can be seen that in the higher energy region the peak around at 3423 cm<sup>-1</sup> is attributed to O-H stretching and the peak appeared at 1614 cm<sup>-1</sup> is assigned to bending (H-O-H) vibration of the water absorbed on the surface of CdS [11]. The absorption band at 663 cm<sup>-1</sup> has been assigned to CdS stretching [12]. There is no vibration for nickel related to peaks, this results again supported that nickel has successfully doped with CdS nanoparticles.



**Fig. 7** FTIR spectrum of pure CdS and Nickel doped CdS



**Fig. 8** Photocatalytic activity of nickel doped CdS and Pure CdS

### 3.6 Photodegradation of Methylene Blue (MB)

MB was used to evaluate the photocatalytic performance of the nickel doped CdS and pure CdS catalytic samples. 50 mg of catalyst was dispersed in 100 mL of 10 μM MB aqueous solution in 250 mL beaker. After stirring for 30 minutes in dark, the solution was transferred to a photoreactor vessel and visible light ( $\lambda > 400$  nm) from the tungsten lamp (150 mW/cm<sup>2</sup>) at time intervals (15 mins), was withdrawn and the catalyst was separated. The absorbance of the MB was measured at 660 nm respectively to monitor their concentrations. Nickel composite material was degraded 96.7% of methylene blue (MB) in 195 mins. Pure CdS composite material was degraded 97.4% of methylene blue (MB) in 150 mins.

## 4. Conclusion

Nanoparticles of pure CdS and CdS have been synthesized by chemical co-precipitation method. XRD pattern confirms the cubic structure of CdS, with a small shift in the peaks at higher to the incorporation of in the lattice. The optical absorbance spectra of nickel doped CdS nanoparticles exhibited a blue shift in the visible region which is size dependent. The band gap decreases with the addition of a dopant. The strong emission peak at ~560 nm in Ni:CdS clearly shows that the low concentration of dopants does not affect the emission of CdS nanoparticles. Nickel doped CdS material was degraded 96.7% of methylene blue (MB) in 195 mins. Pure material was degraded 97.4% of methylene blue (MB) in 150 mins.

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## About the Conference...

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Dr. A. Leema Rose, Associate Professor, PG and Research Department of Chemistry, Holy Cross College (Autonomous),

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