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Synthesis of Mn^{2+} modified CdS nanoparticles and its application as catalyst in photodegradation of methyl red dye

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Photocatalytic degradation of methyl red dye using Mn(5%) doped CdS nanoparticles was studied.Mn doped CdS nanoparticles was synthesized by microwave assisted solvo thermal method where the chemicals used wereCadmium Acetate [$(CH_3COO)_2Cd$, H_2O], Manganese Chloride [$MnCl_2.2H_2O$] and Sodium Sulfide [$Na_2S.xH_2O$]. X-Ray diffraction(XRD) analysis was carried out in order to analyze the structural dimensions of the synthesized nanoparticles and the average crystallite size has been calculated at the full width half maximum (FWHM) of the diffraction peaks using Debye-Scherer equation and it was found to be around2.3nm. FTIR spectra analysis was done in order to analyze different functional and vibrational groups present in the as synthesized sample of Mn doped CdSnanoparticles.The morphology of sample wasstudied by scanning electron microscope. The aqueous solution of methyl red[$C_{15}H_{15}N_3O_2$] has been prepared and was mixed with the as synthesized Mn doped CdSnanoparticles and was exposed for photocatalytic degradation using 100 W bulb. UV-visible spectra of the light irradiated methyl red solutions were studied at different interval of time and no red shift was observed with increase of exposure time. The intensity of the absorption peak was also found to be reduced with the increasing time interval. The photo degradation of methyl red dye was observed up to 90% at the exposure time of 90 minutes.

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*Keywords:*Photo catalytic degradation, Mn doped CdS nanoparticles, X-Ray diffraction, FTIR Spectra, UV Visible spectra

1. Introduction

In recent years, enormous growth of II-VI compound semiconductor nanoparticles have been observed in the field of tumor detection, petrochemical industries, environmental remediation, agriculture, biochemical application, purification/ water distillation, electronics, electrochemical industries, photo catalysis, energy storage and sensors etc[1-4]. The wide applications of semiconductor materials are due to their variant structural, optical, electrocatalytic,chemical and physical properties which is the result of their unique size, space and structure[5,6]. Cadmium Sulphide(CdS) is one of the most prominent compound semiconductors that have been widely used in thevarious notable areas including biosensing, bio imaging techniques, photovoltaic cells, nanomedicines, molecular pathology, drug delivery, biomolecular detection, in medical fieldsdue to their wide band gap, high photosensitivity and photoconductivity[7-10]. One of the major applications of Mn doped CdS nanoparticles is photo catalysis which allow them to photo degrade organic dyes that can't be degraded by natural processes and are resistant to aerobic degradation. They are generally highly toxic since 90% of the dye contains a median lethal dose (LD50) value greater than 2000 mg /kg [11,12]and are introduced in aquatic system thus endangering life of aquatic animals. So, various wastewater treatments such as coagulation, catalytic degradation, biological / aerobic treatment, ion exchange

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removal, ozonization, photolytic degradation has been introduced [13-18].CdS and other II-VI semiconductor nanoparticles have been synthesized by microwave assisted method for various applications [19-21].

The photo sensitized reaction can be represented in following way:-

$$\text{Organic dye} + 2H_2O \xrightarrow{CdS:Mn} CO_2 + H_2$$

The process of mechanism of waste water treatment is mentioned as follows :-

$$e^- (CB) + h^+(VB) \rightarrow \text{enegy} \quad (a)$$

$$H_2O + h^+(VB) \rightarrow OH + H^+ \quad (b)$$

$$e^- (CB) + O_2 \rightarrow OOH \quad (c)$$

$$OH + \text{pollutant} \rightarrow H_2O + CO_2 \quad (d)$$

$$O^{2-} + \text{pollutant} \rightarrow CO_2 + H_2O \quad (e)$$

In present work we have used Mn (5wt%) doped CdS nanoparticles as a photocatalyst for photodegradation of methyl red dye in presence of 100W bulb.

2. Experimental

2.1. Chemical used

Methyl red dye[$C_{15}H_{15}N_3O_2$] as structure shown in fig1, Cadmium Acetate [$(CH_3COO)_2CdH_20$], Manganese Chloride [$MnCl_2.2H_20$], Sodium Sulfide [$Na_2S.xH_20$] were taken for photodegradation of methyl red using Mn doped CdS nanoparticles. All the chemicals were obtained from CDH and were used without further purification and were of analytical grade.

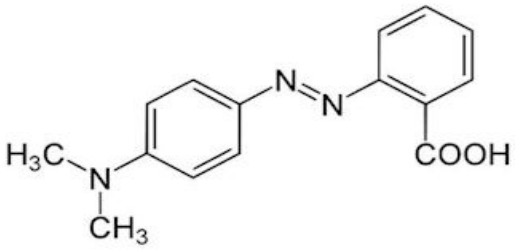

Fig. 1. Structure of methyl red.

2.2.Synthesis of Mn doped CdS nanoparticles

Synthesis of Mn^{+2} doped CdS nanoparticles was carried out in aqueous medium by microwave assisted solvothermal method. The aqueous solution of Cadmium Acetate [$(CH_3COO)_2Cd2H_20$], was mixed stoichiometricallywith aqueous solution of manganese chloride [$MnCl_2.4H_2O$] and was stirred through magnetic stirrer at 700 rpm. The schematic diagram is as shown in fig 1.Theaqueous solution of sodium sulfide [$Na_2S.2H_2O$] was then poured slowly to the above mixed solution and the resultant solution was then undergone through microwave irradiation process where the solution was irradiated for 20sec and relaxed for next 60sec resulting one complete cycle. The resulting yellowish colloidal solution was obtained after 15 cycle. The precipitate was then filtered and dried at 90ºC for 20 hours in an oven to obtain the Mn^{+2} doped CdS nanoparticles.

2.3.Characterization technique

For the characterization, some of the the methods used are as given below:-

(a) X-ray Diffraction (XRD): Using this technique, the sample's X-ray diffraction patterns were taken using Cu-K radiation with a wavelength (λ) of 1.5418Å. The crystallite size of the nanocrystals was determined using the FWHM of XRD peaks and the Debye-Scherer formula.

(b) Scanning Electron Microscopy (SEM): This tool was utilised to determine morphology of nanoparticles and the instrument model was JEOL- JSM-6390LV.

(c) Fourier Transform Infrared spectroscopy (FTIR): The instrument's model was SHIMADZU-IR PRESTIGE 21, and it was used to record FTIR data for knowing various functional groups.

(d) UV-Visible spectroscopy (UV-Vis): Using a RAYLEIGH UV 2601 spectrophotometer, optical absorption measurements in the UV-Visible region (300-800 nm) were recorded.

3. Result and discussion

3.1.X-RAY Diffraction (XRD)

The structural properties of as synthesized Mn^{+2} doped CdS nanoparticles have been studied by XRD analysis. It is a primarily technique used for phase identification and can also provide a unit cells dimension. The major peaks in the spectrum of Mn doped CdS nanoparticles as shown in fig 2 have been observed at 2θ equals 27.5°, 44.5° and 52° which attribute to corresponding hkl value as (111), (220) and (311). The average crystallite size has been calculated at the full width half maximum (FWHM) of the diffraction peaks using Debye-Scherer equation as mentioned in equation (1).

$$D = \frac{k\lambda}{\beta Cos\theta} \quad (1)$$

where, $k$is the particle shape factor (taken 0.9), λ is X-ray wavelength (1.5418 Å), β is FWHM value and θ is the angle of diffraction. The average crystallite size was found to be 2.35 nm for Mn doped CdS nanoparticles.

The inter planer spacing d can be calculated using Bragg's law as given in equation (2)

$$n\lambda = 2dSin\theta \quad (2)$$

wheren is the order of diffraction,λ is the X-Ray wavelength (1.5418 Å), d is the inter planer spacingand$\theta$is the angle of diffraction. The value of inter planer spacing is d

$$d = a/(h^2 + k^2 + l^2)^{1/2} \quad (3)$$

The other important structural parameter is calculated via following equations:

$$\text{Microstrain, } \varepsilon = \frac{\beta Cos\theta}{4} \quad (4)$$

$$\text{Dislocation density } \delta = 1/D^2 \quad (5)$$

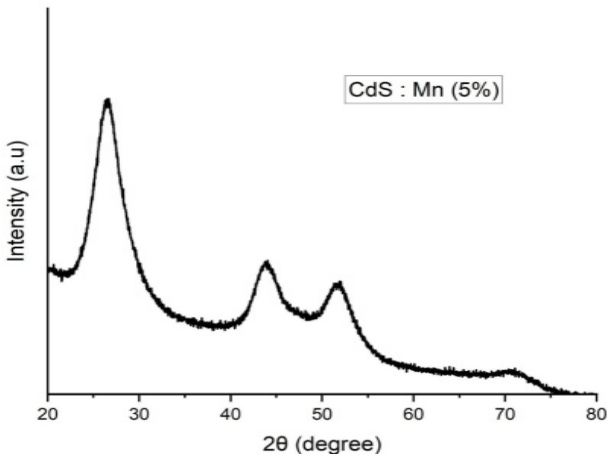

Fig. 2. XRD for Mn doped CdS.

The structural parameter of Mn doped CdS nanoparticles including Interplanar spacing, FWHM, Lattice constant, Macrostrain, Crystallite size, Dislocation density is given in Table 1. The lattice constant, macrostrain, crystallite size, shows the increasing trend with the increase in 2-theta and interplanar spacing trend to decreasing in increase of 2-theta.

Table 1. Different parameter (interplanar spacing, lattice constant, volume, micro strain,dislocation density, Average crystallite size) of Mn doped CdS nanoparticles.

Compound	Interplanar Spacing'd' (Å)	Lattice Constant 'a' (Å)	Volume of unit cell $(Å)^3$	Macro-Strain(ε)	Dislocation density(δ), $(nm)^{-2}$	Average Crystallite Size(nm)
CdS: Mn doped 5%	2.4013	5.842	199.048	0.0271	0.001836	2.35

3.2. FTIR spectroscopy

The different functional and vibrational groups present in the as synthesized sample of Mn doped CdS nanoparticles has been identified by the FTIR Spectra (SHIMADZU-IR-Prestige21) recorded from 400 to 4000cm^{-1} at room temperature. The FTIR Spectra of Mn^{+2} ion doped (5%) CdS nanoparticles Sample is shown in fig 3. Weak absorption band around 3400-3600 cm^{-1} is assigned to the presence of OH stretching vibration of water molecules and moisture present in the prepared sample. The absorption peak around 2800-2900cm^{-1} is assigned to C-H stretching.The small and weak peak around 1600cm^{-1} is due to the presence of H-O-H bending vibration of water molecules. The medium strong band position in the range of 1000-1150cm^{-1} are possibly due to stretching vibration of sulphate group. The sharp peak around 615-625cm^{-1} corresponds to Cd-S and Mn doped CdS stretching.

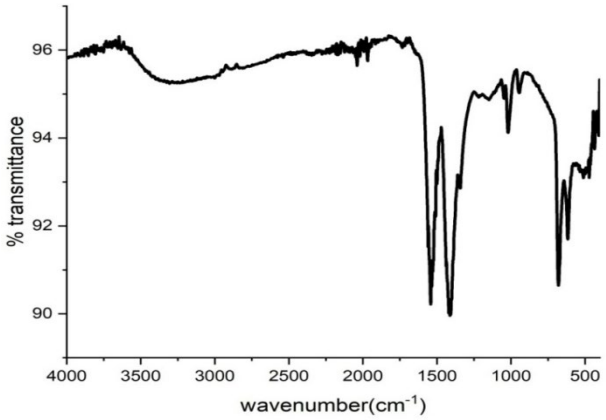

Fig. 3. FTIR OF 5% MndoppedCdS

3.3. SEM analysis

SEM characterization of Mn doped CdS nanoparticles was made by JEOL Model JSM - 6390LV. Fig 4a and. 4b depictthe surface morphology of the nanoparticles which has been taken by SEM. The figures clearly indicate that the synthesized nanocrystals have smooth surface and seems to be spherical. However it is also observed that Mn doped CdSnanocrystalsare highly aggregated which may be due to the absence of capping agent in the synthesis process.

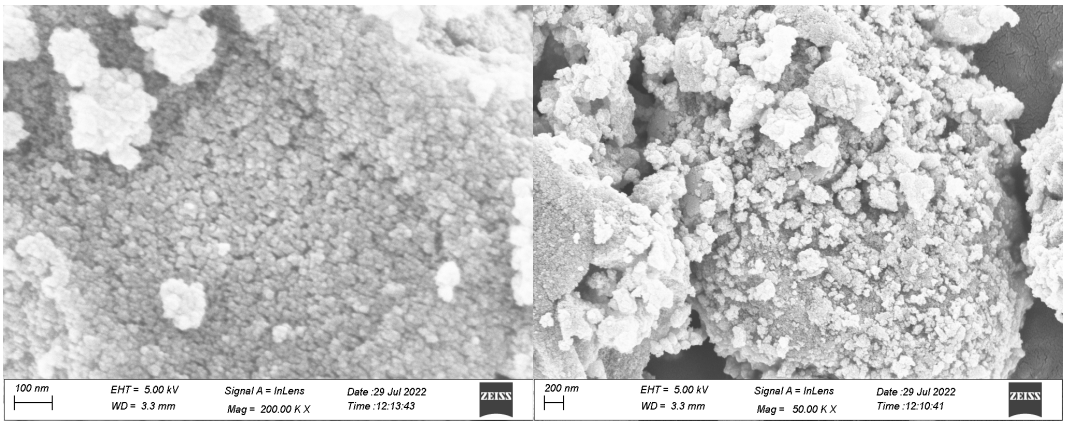

Fig. 4a. SEM image ofMndoppedCdS *Fig. 4b. FTIR OF 5% MndoppedCdS*

3.4. UV-visible spectroscopy

The optical properties of the synthesized sample was studied by using UV-Visible spectrophotometer from the range varying between 200 nm to 800 nm at room temperature. The optical absorption spectra of Mn(5%) doped CdS nanoparticles as well as band gap calculation was made which is shown in figure 5. The optical bandgap of the prepared nanoparticles were calculated by Tauc equation, which is given by equation (5).

$$\alpha h\nu = A\,(h\nu - Eg)^{n} \tag{5}$$

where α is the absorbance,Eg is the bandgap value,hν is the the energy of incident photon, A is a constant and the value of n is taken to be ½ for direct bandgap. And the absorption coefficient (α) is estimated by the equation given below:

$$\lambda\alpha = 4\pi k \tag{6}$$

The bandgap is calculated by extrapolating the graph of $(\alpha h\nu)^2$ versus hν as shown in the fig.5.

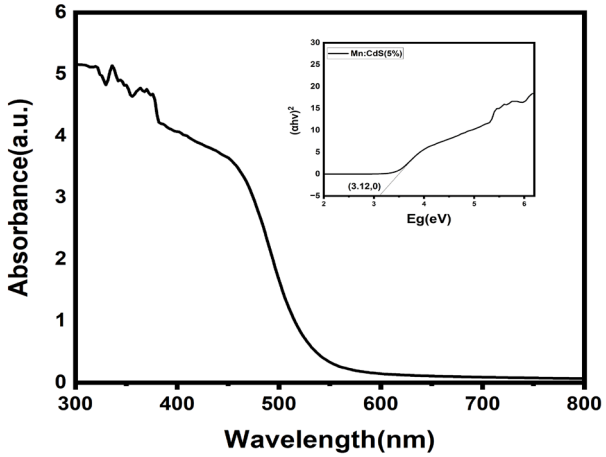

Fig.5. Absorption spectra and energy bandgap of MndoppedCdS nanoparticles.

The extrapolation of the straight line toX- axis gives the value of the bandgap (in eV). The optical bandgap of Mn doped CdS is found to be 3.12 eV. It is clearly seen that the optical bandgap of Mn doped CdS nanoparticles increases from that of the bulk CdS.

3.5. Photocatalytic study

The optical absorption spectra of methyl red dye mixed with Mn doped CdS nanoparticles have been explored by UV Visible spectroscopy (RAYLEIGH-UV2601). Photocatalysis experiment was performed in presence of 100-watt incandescent bulb which is the equivalent of about 1600 lumens. The absorption spectra of the methyl red dye mixed with Mn doped CdS nanoparticle is recorded in the range 200-800 nm at every 15 minutes of exposure time and the variation in the absorbance was recorded. The absorption spectra with variation of time interval have been shown in fig 6.

As per the Beer–Lambert law, the concentration of MR is proportional to absorbance of it and hence, the degradation efficiency of MR can be obtained from equation as given below.

$$R = \frac{A_0 - A_t}{A_0} \times 100\%$$

where A_0 and A_t are the absorbance of MR at the reaction time of 0 and t respectively.

The aqueous solution of methyl red dye was prepared on magnetic stirrer in dark in order to make the solution homogeneous. Further Mn doped CdS nanoparticles was mixed to the solution and stirred at 700 rpm. Methyl red dye mixed with nanoparticles solution was then exposed to 100-watt bulb and the absorbance of the solution was recorded at a fixed interval of time using UV-Visible spectrophotometer. It has been observed that the rate of photo degradation increases with exposure of light and it goes upto 87.5% at exposure time of 90 minutes. Also the maximum intensity peak is shifting towards lower wavelength region.

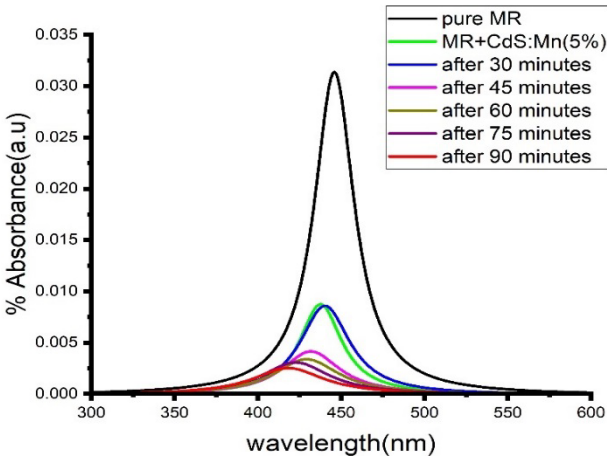

Fig. 6. Absorption spectra of MR dye mixed with NPs with various exposure time.

3.6. Energy-dispersive X-ray analysis

For characterising nanomaterials, X-ray characterization techniques such as small-angle X-ray scattering, X-ray absorption fine structure (XAFS), X-ray diffraction, and X-ray photoelectron spectroscopy (XPS) are used.Energy-dispersive X-ray analysis (EDX) is used in conjunction with SEM to evaluate the types and quantities of elements at the nanomaterial surface or near the surface to give a sample map. The electron beam is transported across the sample during EDX analysis to form an image of the elements in the sample.Fig 6 and 7 show the selected area image and EDX spectra of Mn doped CdS nanoparticles. Table 2 gives the compositional analysis of the as synthesized samples. The EDX analysis result clearly shows the presence of Cd, Mn and S in the sample in proportionate ratio.

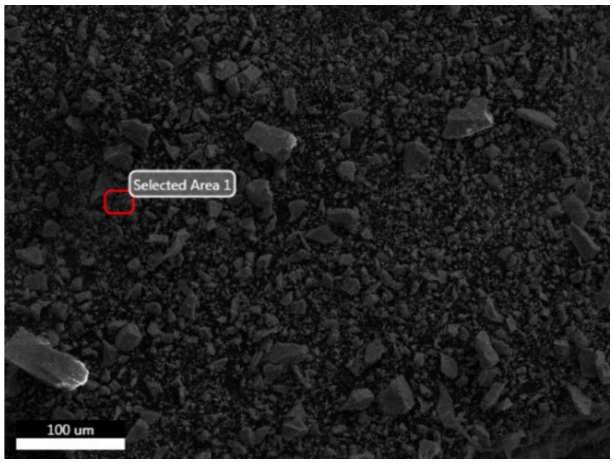

Fig. 7. EDAXanalysis of the prepared samples

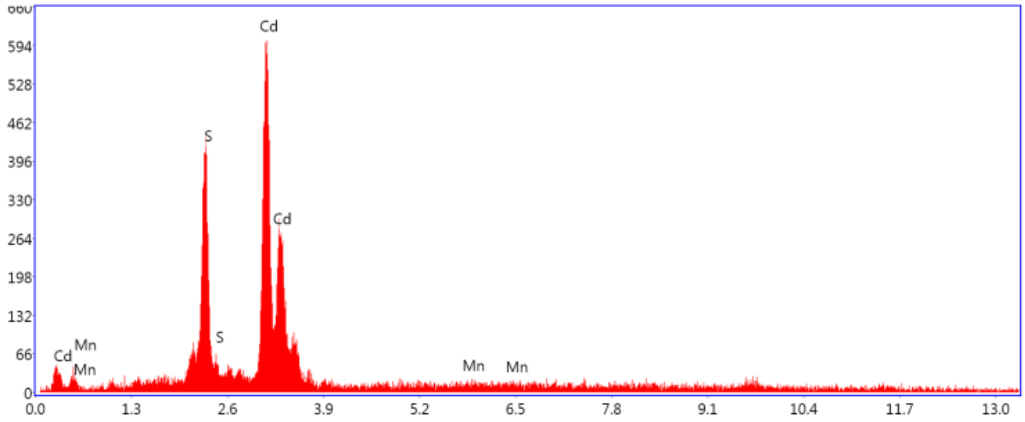

Fig. 8. Energy dispersive x- ray spectra (EDX) of CdS:Mn (5wt %).

Table 2. EDX compositional analysis of the prepared samples.

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
S K	20.53	47.16	142.14	5.61	0.1967	1.2437	0.8643	0.7489	1.0290
CdL	78.40	51.39	213.06	3.98	0.7034	0.9359	1.0530	0.9457	1.0139
MnK	1.08	1.45	2.62	62.50	0.0102	1.0759	0.9340	0.8488	1.0387

4. Conclusion

Microwave aided solvo thermal technique was used to synthesize Mn (5%) doped CdS nanoparticles for photocatalytic degradation of methyl red dye. Major peaks in the spectrum of Mn doped CdS nanoparticles have been detected at 2θ equals 27.5°, 44.5°, and 52°, which are indicative of the structural characteristics of as-synthesized Mn+2 doped CdS nanoparticles. At the diffraction peaks using full width half maximum (FWHM), the average crystallite size 2.35 nm was computed.The prepared samples had an optical band gap of 3.12 eV. The optical characteristics of the produced sample were examined using a UV-Visible spectrophotometer from 200 nm to 800 nm at room temperature. Mn doped CdS nanoparticles have been characterized by the FTIR Spectra obtained from 400 to 4000cm^{-1}.The absorbance of pure methyl red is found at the wavelength 438 nm. A photocatalysis experiment was carried out in the presence of a 100-watt

incandescent bulb, exposing (Methyl red with CdS: Mn doped (5%)) at 15-minute intervals, and it was observed that both the wavelength and absorbance were reduced with the increase of exposure time. The photodegradation of methyl red dye was observed up to 87.5% at the exposure time of 90 minutes. The graph show that the there a slight blue shift as time increases.

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