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## Research Article

### PHOTODEGRADATION STUDIES OF MN DOPED CDSE QDS ON BRILLIANT GREEN DYE UNDER SUNLIGHT IRRADIATION

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#### ABSTRACT

The CdSe QDs doped with Mn (5%) ions was synthesized by chemical precipitation method using the aqueous route. The prepared QDs were characterized by XRD and UV-Vis absorption spectroscopy. XRD results show that the prepared samples were in zinc blende cubic phase. In UV-Vis studies, the absorption spectra of the prepared samples were strongly blue shifted with respect to their bulk counterpart due to quantum confinement effect. The photocatalytic activities of the undoped and Mn (5%) doped CdSe QDs were evaluated by the degradation of Brilliant Green (BG) dye under sunlight irradiation. The photocatalytic experiment confirms that the Mn (5%) doped CdSe QDs exhibit improved photocatalytic efficiency compared to pure CdSe QDs.

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#### INTRODUCTION

Colloidal doped semiconductor nanocrystals (doped quantum dots) have drawn considerable attention in recent years for their size dependent physical and chemical properties [1]. These novel properties render them desirable for various technological applications in a wide range of fields, including optoelectronics, catalysis, photovoltaics and biomedicine [2-7]. So far, various semiconductor materials such as TiO<sub>2</sub>, ZnO, CdS, etc., have been previously investigated for their photocatalytic activity, but these materials possess high band gap energies which result in a significant disadvantage [8]. The band gap energies of TiO<sub>2</sub>, ZnO, and CdS are 3.0 eV, 3.4 eV and 2.4 eV, respectively [9-14]. But cadmium selenide (CdSe) is an n-type semiconductor and its bandgap energy is 1.74 eV. Moreover, CdSe has been found to be suitable for various optoelectronic applications such as light-emitting diodes, laser diodes, catalysis, solar cells and biological labeling [15, 16].

CdSe is also favourable to photocatalytic reactions as photocatalyst due to its wide absorption of visible light with respect to particle size. Typically, the degradation of organic dyes such as Brilliant Green in aqueous suspension is used to evaluate the photocatalytic activity of the CdSe QDs. Also, the dopant ions offer a way to trap the charge carriers which result in better photocatalytic activity of the material [17]. In the present work, a simple chemical precipitation method used for the synthesis of undoped and Mn (5%) doped CdSe QDs with a

view to tailoring their optical properties and the photocatalytic degradation properties of BG dye under sunlight irradiation.

#### MATERIALS AND METHOD

##### Chemicals

The precursor materials of cadmium acetate dihydrate (Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O), selenium (Se) powder, sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>) and manganese acetate dihydrate (Mn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O) were purchased from SD Fine Chem. Limited, India. All the chemicals were of analytical reagent grade and used without any further purification. Deionized water was used for all sample preparations.

##### Preparation of sodium selenosulfate (Na<sub>2</sub>SeSO<sub>3</sub>) solution

For the preparation of Na<sub>2</sub>SeSO<sub>3</sub> solution, 3.78 g of sodium sulphite was mixed with 100 ml of deionized water in a three neck flask at 80 °C, 0.39 g of Se is added to this mixture and then flask quickly purged with nitrogen gas to create an inert environment. After 5 hrs, the colourless sodium selenosulfate solution is formed.

##### Synthesis of undoped and Mn doped CdSe QDs

In a typical synthesis, 1.06 g of cadmium acetate dihydrate is added in 50 ml deionized water and stirred magnetically. While stirring, the prepared sodium selenosulfate solution is added drop by drop and carried out the reaction at 80 °C for 3 hrs. At the end of the reaction, the formed CdSe product is washed

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with deionized water and ethanol to remove the impurities present it. The purified sample is dried at 100 °C for 5 hrs in hot air oven. For Mn doped CdSe sample, 5% of manganese acetate dihydrate is mixed with cadmium acetate dihydrate aqueous solution and then follows the same procedure.

#### Procedure for photocatalytic degradation of Brilliant Green dye

The photocatalytic activity was studied by measuring of BG dye solution degradation under sunlight. The BG dye stock solution was prepared by dissolving 10 mg of BG dye in 1000 mL deionized water. The different weights (10, 20, 30, 40 and 50 mg) of CdSe QDs were added to the 100 mL of BG dye solution and stirred magnetically, which kept under sunlight irradiation. Among the different weights of CdSe QDs, 30 mg was chosen as an optimum for photocatalytic studies. The Mn (5%) doped CdSe QDs was also studied against the BG dye degradation. The BG dye degradation was monitored through different time intervals (15, 30, 45, 60, 75 and 90 minutes). All the experimental works were carried out between 11.00 am and 2.00 pm under sunlight and so that the solar intensity ( $1250 \times 100 \text{ Lu} \pm 100$ ) was maintained as constant.

#### Characterizations

The X-ray diffraction patterns of the synthesized samples (undoped and Mn (5%) doped CdSe) were recorded using a X'PERT-PRO diffractometer with Cu K $\alpha$  (1.54060 Å) at room temperature. The optical absorption spectra of the synthesized samples were recorded by SHIMADZU-UV 1800 spectrophotometer.

## RESULTS AND DISCUSSION

#### Structural studies

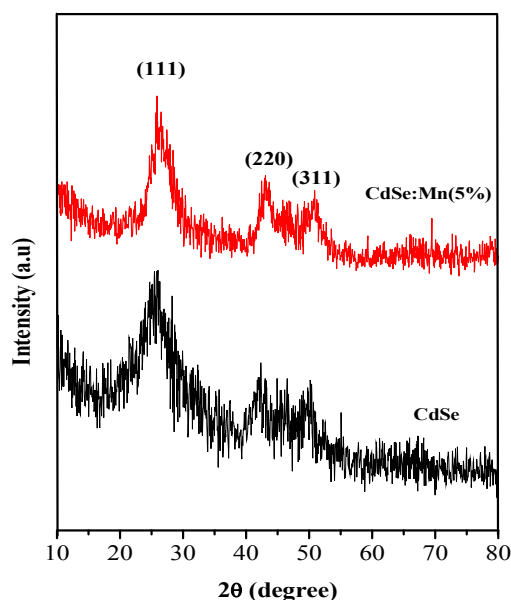


Fig. 1 XRD spectra of undoped and Mn (5%) doped CdSe QDs.

Fig. 1 shows the XRD spectra of undoped and Mn (5%) doped CdSe QDs. The XRD pattern for CdSe show the reflection angles ( $2\theta$ ) at  $25.5^\circ$ ,  $42.0^\circ$  and  $49.8^\circ$  belong to the main diffraction peaks can be indexed to (111), (220) and (311) planes, indicating that the formation of zinc blende cubic

phase of CdSe (JCPDS card No: 19-0191). Moreover, No other peaks are detected to impurities, denoting that the high purity of CdSe product. The crystal structure of CdSe QDs was not affected by the dopant Mn $^{2+}$  ions. Also, the broadness of XRD peaks is caused by the nano size effect. In addition, the XRD peak of Mn (5%) doped CdSe QDs was slightly shifted to higher angles when compared to undoped CdSe QDs, indicating the presence of dopant Mn ions in the CdSe matrix. The lattice constant for undoped CdSe QDs is 6.0630 Å and CdSe: Mn (5%) is 6.0457 Å. The decrease in lattice constant for Mn doped CdSe QDs is due to the replacement of Cd $^{2+}$  ions by Mn $^{2+}$  ions since the ionic radius of Cd $^{2+}$  (0.92 nm) is greater than the Mn $^{2+}$  (0.81 nm). The mean particle size of the undoped and Mn (5%) doped CdSe QDs was estimated by Scherrer's equation [18, 19].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad \dots (1)$$

Where k is a constant ( $k = 0.9$ ),  $\lambda = 1.54060 \text{ \AA}$  (Cu K $\alpha$  radiation wavelength),  $\beta$  is full width at half maximum and  $\theta$  is the Bragg's angle. The estimated mean crystallite size for undoped and Mn (5%) doped CdSe QDs are 4.4 and 3.0 nm, respectively. It can be seen that the size of the synthesized undoped and Mn doped CdSe particles are smaller than Bohr exciton radius of CdSe (5.6 nm) [20], confirming that the synthesized particles are quantum dots.

#### Optical studies

Fig. 2 shows that the UV-Vis absorption spectra of undoped and Mn (5%) doped CdSe QDs. It can be seen that the absorption edges appeared at around 583 and 543 nm in the absorption spectra of undoped and Mn (5%) doped CdSe QDs, respectively. The absorption edges were strongly blueshifted when compared to the bulk CdSe (716 nm). [21]. This strong blue shift in the absorption spectra of both undoped and Mn (5%) doped CdSe samples, indicating that the synthesized particles must be smaller than the exciton Bohr radius of CdSe [22].

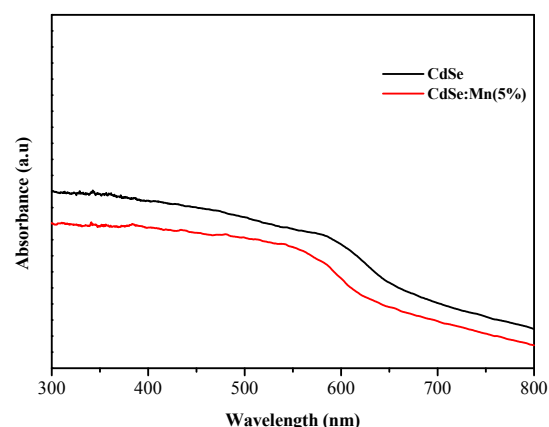


Fig. 2 UV-Vis absorption spectra of undoped and Mn (5%) doped CdSe QDs.

It is known that the fundamental absorption is due to the electron excitation from the valance band to the conduction band and used to estimate the optical bandgap of the synthesized undoped and Mn doped CdSe QDs. The band gap

( $E_g$ ) of the synthesized QDs can be estimated by the following simple expression,

$$E = h\nu \quad \dots (2)$$

Where  $h$  is Planck's constant ( $6.626 \times 10^{-34}$  J s),  $\nu = c/\lambda$ ,  $\nu$  is the absorption frequency,  $c$  is the velocity of light ( $3 \times 10^8$  m/s) and  $\lambda$  is the absorption wavelength. The band gap values for undoped and Mn (5%) doped CdSe QDs are 2.12 and 2.28 eV, respectively, which are higher than the band gap of bulk CdSe ( $E_g^{\text{bulk}} = 1.74$  eV) [23]. This observed shift in the bandgap to higher energy due to the quantum confinement effect [24-28]. The enhancement in the band gap was caused by the reduced particle size as well as the incorporation of Mn dopants into the CdSe lattice.

**Photocatalytic studies on BG dye degradation**

The photocatalytic activities of the undoped and Mn (5%) doped CdSe QDs were evaluated by the degradation of the BG dye under sunlight irradiation. The absorption spectra of exposed QDs samples at different time intervals were recorded. The rate of degradation was analyzed by monitoring variation in the intensity of the BG absorption band at 624 nm.

The absorption spectra (Fig. 3 (a) and (b)) show the spectral change in the absorbance of BG dye during the photocatalysis at the time interval of 15 min. It can be seen that the intensity of the absorption band at 624 nm of BG steadily decreases in both QDs samples.

After about 90 minutes of sunlight irradiation, the intensity of the absorption band in CdSe QDs (Fig. 3 (a)) decreased to about 81.9 % while the intensity of the absorption band in Mn (5%) doped CdSe QDs (Fig. 3 (b)) decreased to about 86.5 %. This indicates that the Mn (5%) doped CdSe QDs decolorizes BG dye faster than undoped CdSe QDs.

The degradation percentage was calculated using the following relation [29],

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad \dots(3)$$

Where  $C_0$  is the initial concentration and  $C_t$  is the dye concentration at time 't' from the start of the photocatalytic reaction.

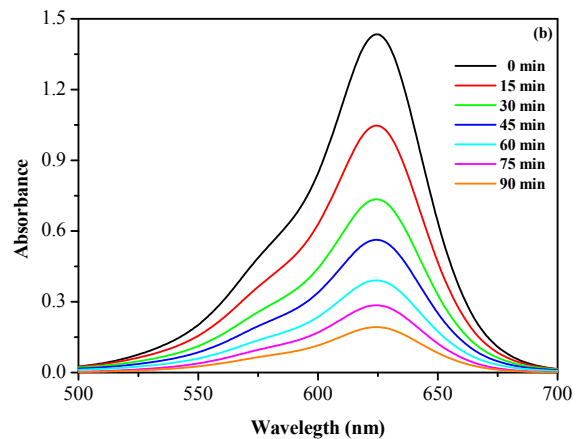
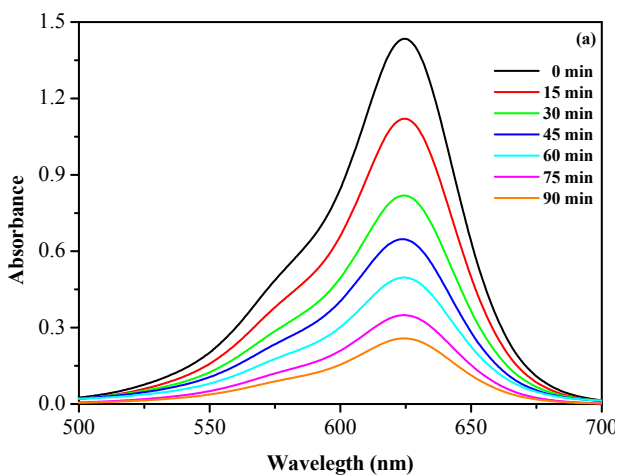


Fig. 3 UV-Vis absorption spectra of BG dye for (a) undoped CdSe QDs and (b) Mn (5%) doped CdSe QDs under sunlight irradiation at different time intervals.

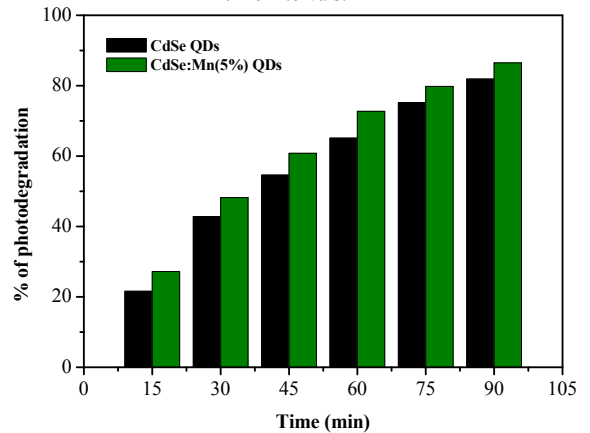


Fig. 4 Variation of photocatalytic degradation (%) vs. time.

Fig. 4 shows the variation of the photocatalytic degradation (%) versus time. The photocatalytic activity of Mn (5%) doped CdSe QDs is higher when compared to the undoped CdSe QDs. This is due to the charge carrier trapping process is more probable than charge recombination and thus surface charge transfer probability. In addition, the enhanced photocatalytic activity may be due to the smaller particle size as compared to undoped photocatalyst. Therefore the surface to volume ratio for Mn (5%) doped CdSe QDs is higher, which offer more surface active sites results in the enhancement of photocatalytic performance.

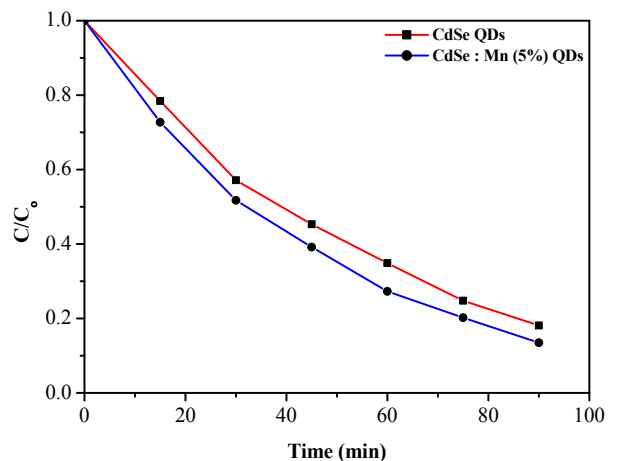


Fig. 5 Concentration ratio of  $C/C_0$  with different time intervals for photocatalytic degradation of BG dye under sunlight irradiation.

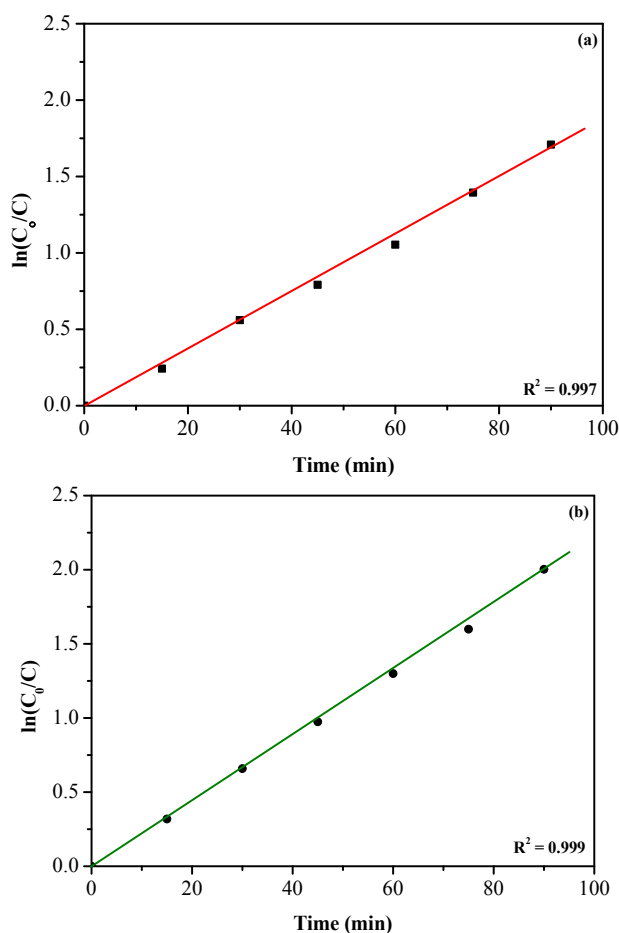
Moreover, when the size of particles decreases, the amount of the dispersion of particles per volume in the solution will increase, which resulting in the increase in a number of active sites of the photoactive center. **Fig. 5** shows the temporal concentration changes of BG for the undoped and Mn (5%) doped CdSe QDs.

The photocatalytic degradation of BG dye by undoped and Mn (5%) doped CdSe QDs of the reaction solution obeyed the pseudo-first-order kinetics. The simplest representation for the rates of photodegradation of BG dye is given by the following equation

$$\ln C = -k t + \ln C_0 \quad \dots (4)$$

This equation can be used to demonstrate linearity of data if the integration of eq. (4) is given by

$$\ln \left( \frac{C_0}{C_t} \right) = k t \quad \dots (5)$$



**Fig. 6** A plot of  $\ln(C_0/C)$  vs. Time interval for photocatalytic degradation of BG dye under sunlight for (a) undoped CdSe QDs and (b) Mn (5%) doped CdSe QDs.

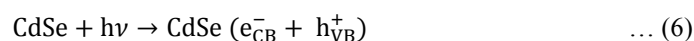
Where  $k$  is the constant of the pseudo-first-order rate. The reaction kinetics revealed by the plot of  $\ln(C_0/C)$  versus the sunlight irradiation time ( $t$ ) is shown in **Fig. 6**. The straight lines are obtained, indicating that the reaction is first order.

The calculated rate constant ( $k$ ) for undoped and Mn (5%) doped CdSe QDs are  $0.0190 \text{ min}^{-1}$  and  $0.0222 \text{ min}^{-1}$ ,

respectively. This means that the incorporation of Mn ions in the CdSe host increases the photocatalytic efficiency. The  $\text{Mn}^{2+}$  dopant can serve the charge traps, retarding the electron-hole recombination rate and thereafter enhancing the interfacial charge transfer for BG dye degradation.

#### Photodegradation mechanism

When the photocatalyst CdSe is illuminated with photons of energy equal to or greater than its band-gap energy [30], valence band electrons will be excited to the conduction band producing electron-hole pairs, which diffuse to or near the catalyst surface and is referred to as the semiconductor's photo-excitation state. The production of photoinduced electron-hole can be expressed by the relation



The photo-generated holes move to the surface and react with surface  $\text{OH}^-$  groups and  $\text{H}_2\text{O}$  to produce  $\text{OH}^\bullet$  radicals, which get adsorbed on the CdSe surface (eq. 7 and 8).



These surface adsorbed hydroxyl radicals  $\text{OH}^\bullet$ , which are known to be strong oxidizing species, react with BG dye molecules adsorbed at the surface of catalyst, mineralizing the compound partially or completely according to the equation (eq. 9)



On the other hand,  $\text{O}_2$  plays an important role in these reactions. The electrons in the conduction band can reduce  $\text{O}_2$

to produce superoxide radicals ( $\text{O}_2^\bullet$ ) (eq. 10). Subsequently,

these  $\text{O}_2^\bullet$  radicals react with hydrogen ions generated through

water splitting to form hydroperoxyl  $\text{HO}_2^\bullet$  (eq. 11) radical and other reactive oxygen species such  $\text{H}_2\text{O}_2$  (eq. 12 and 13).



The  $\text{OH}^\bullet$  radicals are the most important oxidants formed in a photocatalytic process responsible for the degradation of BG dye. Therefore the lower recombination rate of the photoexcited electrons and holes prolong the life time of photogenerated carrier and conclude that Mn (5%) doped CdSe QDs are the best photocatalyst in comparison with that of undoped CdSe QDs.

Moreover, the photocatalytic depend on the particle size, which in turn affects the amount and life time of charge carriers. The photocatalytic activity for the undoped CdSe QDs is typically low since size is larger compared to that of Mn (5%) doped CdSe QDs. This low value due to fast recombination of electron-hole pairs.

Whereas in Mn (5%) doped CdSe QDs, the electron-hole inhibition rate from the interface is higher due to a smaller size,

which results in the short transport distance. This indicates that more electron-hole participates in the reaction.

## CONCLUSIONS

In summary, the undoped and Mn (5%) doped CdSe QDs was successfully synthesized by chemical precipitation method using the aqueous route. XRD pattern reveals that the synthesized undoped and Mn (5%) doped CdSe QDs were in zinc blende cubic structure and their sizes were 4.4 and 3.0 nm, respectively. The synthesized QDs were characterized by UV-Vis absorption spectroscopy, which shows that the undoped and Mn (5%) doped CdSe QDs were blue shifted with respect to bulk CdSe due to quantum confinement effect. The photocatalytic activity of BG dye under sunlight irradiation was higher in Mn (5%) doped CdSe QDs than undoped CdSe QDs.

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