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ENHANCEMENT PHOTOCATALYTIC ACTIVITY OF Mn DOPED CdS/ZnO NANOCOMPOSITES FOR THE DEGRADATION OF METHYLENE BLUE UNDER SOLAR LIGHT IRRADIATION

ABSTRACT

In this study, Mn doped CdS/ZnO nanocomposites synthesized by co-precipitation method and its photocatalytic activity was tested using methylene blue under solar light irradiation. The prepared hybrid nanocomposites are characterized by using different physicochemical techniques including XRD, FESEM, EDX, TEM, UV-vis DRS and PL analysis. From the XRD analysis, Mn doped ZnO/CdS nanocomposite diffraction peaks only reflect the binary crystalline structures of ZnO and CdS. However, there is no characteristic peak of Mn is found that may be because of low content of Mn doped on ZnO/CdS. But Mn (2.9 wt%) was detected in the Mn doped ZnO/CdS nanocomposite, which was measured by EDX analysis. The FESEM and TEM results exhibit the surface particle of Mn doped ZnO/CdS nanocomposite which have spherical nature and confirmed the formation of Mn doped ZnO/CdS nanocomposites. The photocatalytic degradation results have revealed that the Mn doped CdS/ZnO nanocomposites exhibit admirable activity toward the photocatalytic degradation of the MB. The reason for excellent photocatalytic activity of Mn doped CdS/ZnO nanocomposites indicates the absorbance band shifted to red region and reduction of recombination of photogenerated electron-hole, which is in good agreement with UV-visible DRS analysis and PL study results. The fitted kinetic plots showed a pseudo-first-order reaction model and the appropriate rate constants were found to be 0.0068 min^{-1} , 0.00846 min^{-1} , and 0.0188 min^{-1} , for ZnO, 25 % CdS/ZnO, and 0.8 mol% Mn doped CdS/ZnO nanocomposites, respectively. The maximum photocatalytic activity was achieved by 0.8 mol% Mn doped CdS/ZnO nanocomposites with a 95% degradation efficiency of MB. Hydroxyl and superoxide radicals, having a vital role in the degradation of MB, confirmed scavenging experiments. In addition, the recycling tests displays that the Mn doped CdS/ZnO nanocomposites have shown good stability and long durability. The enhanced photodegradation activity of Mn doped CdS/ZnO nanocomposites indicates the potential of the nanocomposite for the treatment of organic pollutants from the textile wastewater.

Keywords: *Mn doped CdS/ZnO nanocomposites; methylene blue dye; solar light; dye degradation; TEM analysis*

INTRODUCTION

Water is elixir of life. Though the earth is covered by three fourth of water, still there is a crisis of potable water and clean water for domestic purposes. Pure water resources are one of the essential dire needs of the current age in our daily life. Due to the rapid human population growth,

the increased industrial growth and urbanization pose a great threat to the environment and human beings. The wastes that are released from the all kinds of industries are the major agents of polluting the eco-system resulting in an imbalance in the environment [1]. Particularly, the textile industries use enormous carcinogenic synthetic dyes which are chemically and physically stable. It is very unsafe for the environment. From the stability nature of the manmade dyes, the industrial effluent or wastewater is flown in to the soil [2-4].

In the wood and textile industries, the cationic dyes such as Methylene Blue (MB) are largely used with various applications [5]. Generally MB, present in aquatic medium causes irreparable harms to water bodies. The degradation of MB from wastewater is a major issue because MB degraded unevenly leads to the formation of hazardous chemical species, finally affecting the environment. Nowadays various treatment methods like adsorption [6], biosorption [5] membrane filtration [6] and Fenton process [7] are applied to degrade MB dye. Above mentioned techniques have some limitation due to production of secondary pollutants and waste sludges [9]. These methods are ineffective for complete degradation of huge amount of water soluble and bio importunate type of dyes [10]. From the background discussion, environment-friendly, clean, effective, inexpensive, and efficient treatment process are needed to degrade the methylene blue dye [11]. To achieve this, the photocatalytic technique can be implemented in the degradation of MB dye process [12-14]. Due to its unique advantages without producing secondary pollutants, the recommended photocatalytic technique can also be called Greener and Effective treatment method [15].

The photocatalysis researchers have reported, the semiconductor photocatalysts effectively degrades the organic hazards by the production of highly active species as hydroxyl and oxygen radical [8]. And these active radicals bombard the organic skeleton to produce the photomineralized product like non toxic organic content and inorganic salts. Among the ecofriendly photocatalysts, ZnO is a familiar one because it is an alternative photocatalyst for good guarantee species like TiO₂ [16-18]. But, the development of ZnO photocatalyst has been a great challenge in producing good crystalline nature. Synthesis of ZnO nanoparticles was well-established through numerous physical and chemical approaches, such as precipitation [19], the sol-gel method [20], solvothermal or hydrothermal [21], electrochemical [22] and microwave methods [23]. Eventhough these approaches are direct and feasible, several limitations are recognized through these approaches, including adsorption of traces of toxic chemicals on the synthesized nanoparticles. Among the numerous synthetic procedures [24,25] of nanoparticles proposed by researchers across the world, solvent mixing dispersed co-precipitation method is found to be superior to other methods in many aspects. In this method, the shape and size of massive nanoparticles can be achieved [26]. Recently, polar solvent assisted (solution mixing) synthesis of ZnO nanoparticles has been in high demand due to the reproducible, cost-effective nature. The capability of polar solvent assisted synthesis for the fabrication of nanoparticles is yet to be fully explored. Herein, we have chosen the safer synthesis of ZnO nanoparticles using a polar solvent despised method.

Unfortunately, the ecofriendly ZnO nanoparticles have unusual drawbacks like low utilization of visible light and simultaneously recombine the electron and hole charges. In addition, the wurtzite ZnO is highly affected by the photocorrosion and has leach out property in acidic medium.

In order to minimize the above mentioned drawbacks, ZnO could be modified in its surface and the band structure. These modification techniques are metal ion and nonmetal ion doping, trapping by metal nanoparticles and development of heterostructure between the ZnO and other semiconductor. This modification highly encourages the enhanced visible light absorption in the solar spectrum [27-29]

Among the modification experiments, coupling of heavy metal sulphides enriches the photoresponse and serve as platform to effective charge separation and transport. Based on effective coupling templates, the combination of ZnO and nano CdS [30] pay more attention for the photocatalytic degradation applications in the solar light source [31]. The enhancement activity depends on suitable band gap (2.4 eV) and high optical absorbance coefficient of CdS [32, 33]. Overall the binary nanocomposites show a large variety of benefits like a high charge carrier mobility, heterojunction formation, extended life time of charge carrier, and huge charge separation etc. [34].

Furthermore, metal ion doping or coupled with binary nanocomposites has shown a large dye degradation activity. Based on the above discussion some visible light-driven ZnO/Ag₂MoO₄/Ag nanocomposites [35], Pd deposited ZnO/CuO nanostructures [36], magnetic Ag/ZnO/Fe₃O₄ composite [37] and Fe doped ZnO/CdS nano composite [38] are some of the transition metal and noble metal deposited nanocomposite which show explempory performance in the photocatalytic applications.

On account of the above mentioned facts, polar solvent assisted co-precipitation method is used for the successful preparation of Mn doped CdS/ZnO nanocomposites So the enhancement of photocatalytic activity of Mn doped CdS/ZnO nanocomposites was obtained by facilitating the separation efficiency of photogenerated carriers. The nanostructures, morphologies, surface chemical composition, photocatalytic activity, and possible performance improvement mechanism of Mn doped CdS/ZnO nanocomposites have been researched in detail.

MATERIALS AND METHODS

In this work we have discussed the synthesis and fabrication of nanocomposites, spectral studies and photocatalytic studies.

Materials

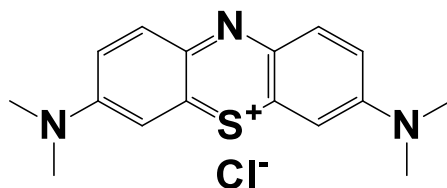
Methylene blue (MB) (Mark, Germany, dye content 85%) was used for photocatalytic degradation studies.

Chemical formula: C₁₆H₁₈ClN₃S

Molecular weight: 319.85 g/mol

Water solubility: 43.6 g/L in water at 25 °C

λ_{max} : 668 nm



Methylene Blue (Phenothiazin- 5-ium, 3,7-bis(dimethylamino)-, chloride)

zinc acetate dehydrate (GR) and potassium hydroxide (GR) manganese acetate (LR), sodium sulfide (LR) cadmium nitrate (LR) and aqueous ammonia (GR) was purchased in Merck India Pvt. Ltd. The double distilled water is used for the preparation dye solution for the photocatalytic

studies. The dye solution of pH was modified with adding NaOH and HCl for basic and acidic nature respectively. Isopropanol, benzoquinone and ammonium oxalate used as trapping agent for measurement of active species.

Synthesis of Mn doped CdS / ZnO Nanocomposites

The Mn doped ZnO/CdS Nanocomposites were prepared by previous method in the mixture of zinc acetate dehydrate and potassium hydroxide (KOH) solution manganese acetate mixed with 50 mL of distilled water is added and vigorously stirred. Followed by this (Cd(NO₃)₂) and sodium sulphide (Na₂S) are added as previous method. The resultant colloidal solution is allowed to stirrer for 3 hours and filtered. Then dried, heated and finally powdered. The prepared sample was referred to as 0.2 mol% Mn doped ZnO/CdS. The Mn²⁺ dopant varied as 0.4 mol%, 0.6 mol%, 0.8 mol% and 1.0 mol%.

Characterization

Philips X'pert-MPD diffractometer used for recorded X-ray diffraction patterns of photocatalysts X-ray powder diffraction (XRD) patterns of the photocatalysts in the 2 θ range 20°–80° using Cu Ka radiation (MRL 1012, 1032 and CNSI (Elings Hall) 1409, California, USA). The correct phase structure of corresponding photocatalysts was determined by experimental X-ray pattern and it was matches the standard compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS). Scanning Electronic Microscopic studies was done by ULTRA55 FESEM, Carl Zeiss and this study is used to measure the morphological characteristics. Transmission electron microscopy was done by using Tecnai F30 operated at 180 kV. Perkin Elmer, Lambda 35 spectrometer (Solid state UV-visible spectrometer) used for analysis of optical absorbance properties. The emission spectra were recorded using perkin Elmer (photoluminescence detector) specifically the excitation wavelength of 325 nm.

Photocatalytic activity test

The photocatalytic activity of prepared photocatalysts has been tested by methylene blue (MB) under solar light irradiation. In a typical procedure, 30 mg of MB dye with aqueous solution were taken in clean 250 ml borosilicate beaker and then 50 mg of photocatalysts has been added in the same solution which is maintain in the ambient conditions. The photocatalytic mixture was kept at dark place to attain the equilibrium (adsorption vs desorption) and further the solution was stirred up to 20 min. Further the solution was place in sunlight source (clear sky atmosphere) for 50 min. To avoid the temperature variation, the reaction setup were placed cooling water bath. During the photocatalytic reaction the dye solution was tested every 10 min intervals in the predicted reaction time. Then this dye solution was centrifuged and measures the concentration of dye solution by using Elico SL-171 visible spectrophotometer. In order to avoid the variation in results due to fluctuation in the intensity of the sunlight, a set of experiments were carried out simultaneously. The active species from photocatalytic mechanism were detected by using the same procedure in the presence of scavengers.

The percentage of degradation was calculated using the following relations:

$$\% \text{ of Degradation} = \left(\frac{C_0 - C}{C_0} \right) \times 100$$

Where C_0 is the initial concentration of the dye solution, C – the concentration of the dye remains after degradation. The same procedure followed all the photocatalytic experiments.

RESULTS AND DISCUSSION

Crystalline phase identification

The X-ray diffraction analysis was used to identify crystalline structure and crystalline phase of all the prepared samples. The diffraction patterns are shown in Figure 1. The location of 2 theta values at $\theta = 31.78^\circ$, 34.32° , 36.2° , 47.48° , 56.43° , 62.84° , 67.92° , 69.02° , 72.46° and 76.98° specifically corresponds to the plane (100), (002), (101), (102), (110), (103), (112), (201), (004) and (202) which is represented by the pure ZnO as hexagonal wurtzite phase (JCPDS-00-036-1451). The CdS crystal structure also exactly matches with the JCPDS card no.89-2944 and also it possesses better crystalline structure.

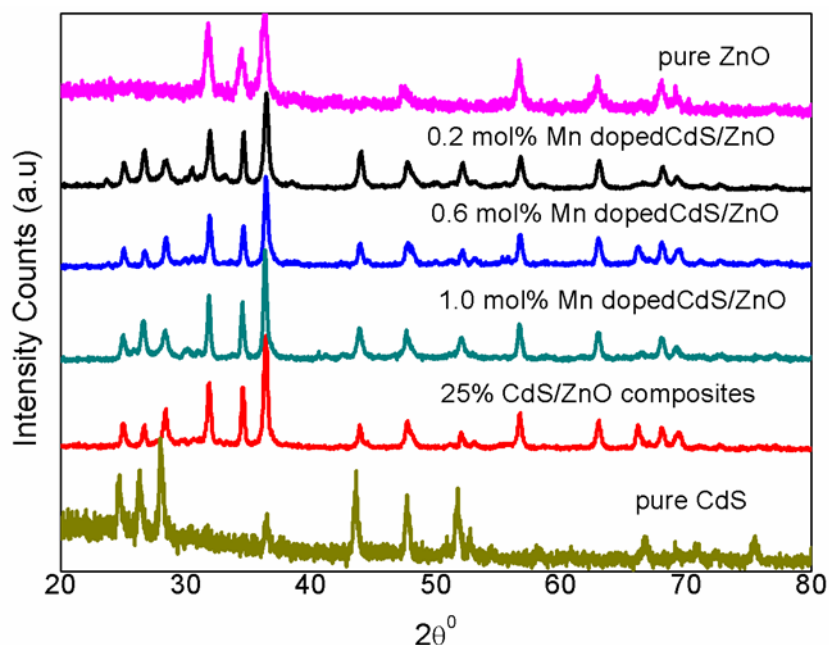


Fig. 1. XRD patterns of pure ZnO, CdS, 25 % CdS/ZnO binary composites, 0.2 mol% Mn doped CdS/ZnO, 0.8 mol% Mn doped CdS/ZnO and 1.0 mol% Mn doped CdS/ZnO nanocomposites

The diffraction pattern of 25 % CdS/ZnO binary nanocomposites (Figure 1) shows all the major peaks of CdS and ZnO. In addition, the CdS peaks have less intense in the binary composites. The reason is one fourth concentrations of CdS, fabricate with ZnO crystalline phase and also the CdS has low crystallinity than that of ZnO. Furthermore, no impure peaks appear in the CdS-ZnO nanocrystalline plane which confirms the formation of CdS/ZnO binary composites. In Mn doped ZnO/CdS nanocomposite, the diffraction peaks only reflect the binary crystalline structures of ZnO and CdS. However, there is no characteristic peak of Mn is found that may be because of low content and weak intensity of Mn. Further, an increase in Mn amount on CdS/ZnO binary structure, intensifies the diffraction peaks gradually which indicates that the high crystallinity of

nanocomposites only doping of transition metal (Mn). This type of crystalline behavior of CdS/ZnO binary composites may be responsible for better photocatalytic catalytic activity [38].

Surface property analysis

The field emission scanning electron microscopic (FESEM) study was used to analyze surface morphology and particle size of prepared nanocomposites. It is shown in Figure 2. The synthesized pure ZnO has largely agglomerated the spherical shape and this spherical dot size was eventually 55 nm (Fig. 2a). The FESEM image of CdS/ZnO binary nanocomposites (Fig. 2b) exhibited round pallets with highly dispersed surface. In addition some agglomerated surface area was also observed with 50 nm sized pallets. Figure 2c demonstrates the FESEM image of 0.2 mol % Mn doped CdS/ZnO nanocomposite, which displays a new morphology of nanosurface like a spherical pillar. This indicates manganese ion located in the lattice of CdS/ZnO and this type of morphology may pronounced a controllable synthetic route [39].

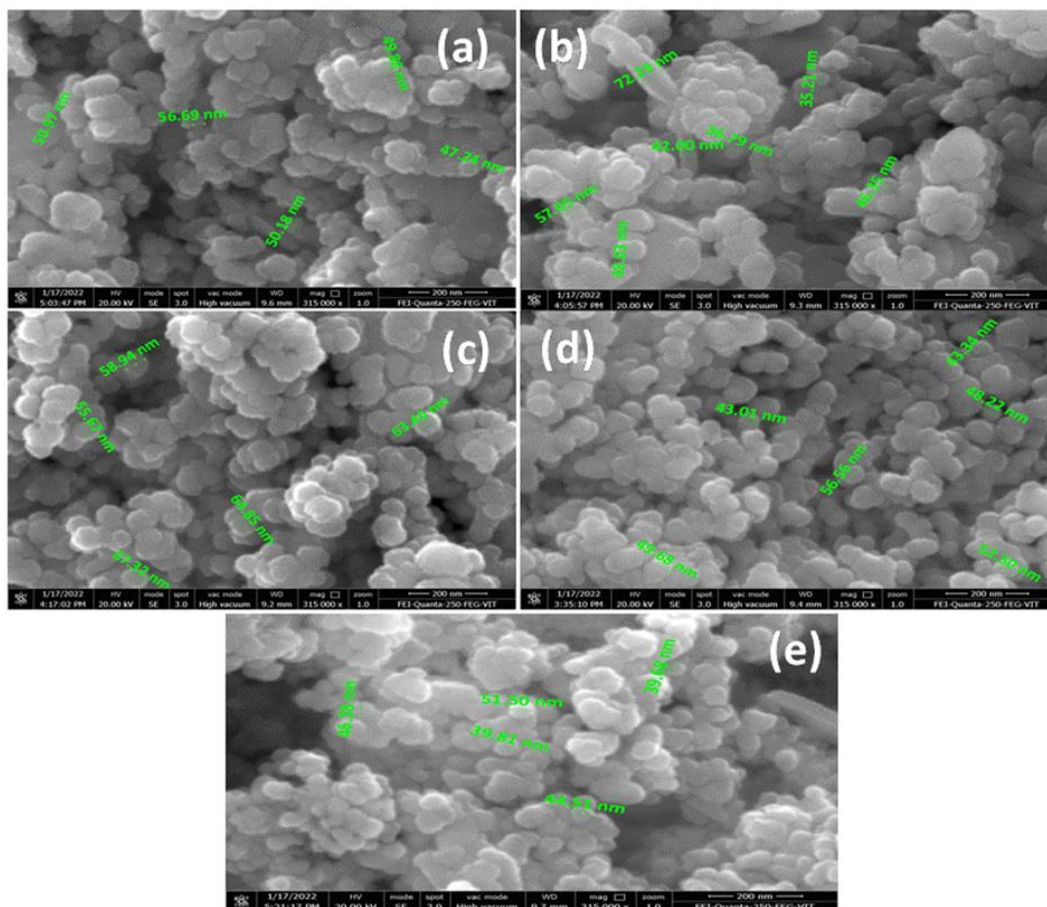


Fig. 2. FESEM images of pure ZnO, 25 % CdS/ZnO binary composites, 0.2 mol% Mn doped CdS/ZnO, 0.8 mol% Mn doped CdS/ZnO and 1.0 mol% Mn doped CdS/ZnO nanocomposites

The typical FESEM micrographs of 0.8 mol% Mn doped CdS/ZnO nanocomposites are shown in Figure 2d. This Mn doped CdS/ZnO nanocomposites show uniform size and high porosity surface [40]. This surface may highly suitable for adsorption of substrate (dye). Further, incorporation of Mn^{2+} ion (1.0 mol%) into the CdS/ZnO binary nanocomposites, changes the

morphology of nanocomposites as blurred agglomerated surface and is clearly depicted in Figure 2e. The irregular agglomerated surface shows larger particle size due to excess amount of dopant (Mn) into the CdS/ZnO binary nanocomposites.

Elemental composition analysis

The elemental composition of fabricated Mn doped CdS/ZnO nanocomposites is determined by EDX, a micro analytical technique used in association with SEM. The EDX detects X-rays emitted from sample when electrons are bombarded on material surface. Data about chemical composition is provided by measuring the intensity and energy of the signal. The EDX spectrum shows frequency of X-rays in counts for each energy level. The intensity of the peak gives information about the amount of the element in sample [41]. Figure 3a represents EDX spectra of CdS/ZnO binary nanocomposites. The weight percentage of Zn, O, Cd and S elements present in the appropriate amounts like 39.8, 24.3, 16.3 and 3.6 wt % respectively. These results indicate high amount of ZnO present in the CdS/ZnO binary nanocomposites than the CdS. Figure 3b represents that Mn doped CdS/ZnO nanocomposites, contains 2.9 wt% of Mn with considerable amount of major components with their targeted chemical composition (Zn, Cd, O and S). It was confirmed that Mn is present along with ZnO and CdS in the binary composite. In addition some impurities like Na and K are also present in Mn doped CdS/ZnO nanocomposites. These impurities may arise from synthetic process while using glass apparatus. Overall EDX result, indicates there is no unwanted impurities present in the prepared samples.

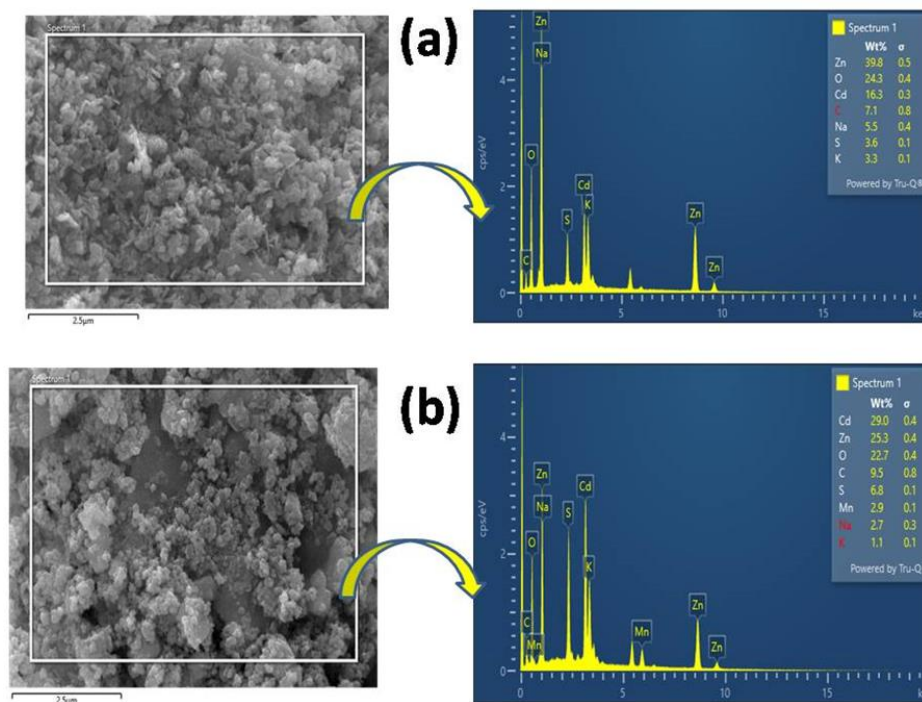


Fig. 3. EDX spectra of (a) CdS/ZnO binary composites and (b) Mn doped CdS/ZnO nanocomposites

Surface particle structure analysis

TEM images were obtained to determine the particle size, morphology and crystal structure of Mn doped CdS/ZnO nanocomposites. Fig. 4(a) and (b) show that the average size of Mn doped CdS/ZnO nanocomposites is approximately 50 nm, which is much smaller than the ZnO. Figure

4a shows that the surface particle structure of the Mn doped a CdS/ZnO nanocomposite which is present in a spherical stacked structure. Further, Mn, CdS and ZnO are stacked in close contact with each other. The dense small spherical dot in Figure 4 b represents the Mn ion incorporated uniformly to the CdS/ZnO nanocomposites surface. This TEM results, indicate the Mn doped binary CdS/ZnO nanocomposites was successfully composited. From the fringe analysis results (Figure 4c,) the lattice spacing value of the ZnO (002) crystal plane is 0.26 nm [42]. Moreover, the selected area electron diffraction (SAED) pattern of Mn doped CdS/ZnO nanocomposites (Fig. 4d) reveals a ring-like pattern, indicating the low crystalline nature of Mn doped CdS/ZnO nanocomposites. The SAED pattern (Figure 4d) indicates that the polycrystalline form of the material, and the reflection planes obtained are very much in alignment with the information deduced from the XRD pattern.

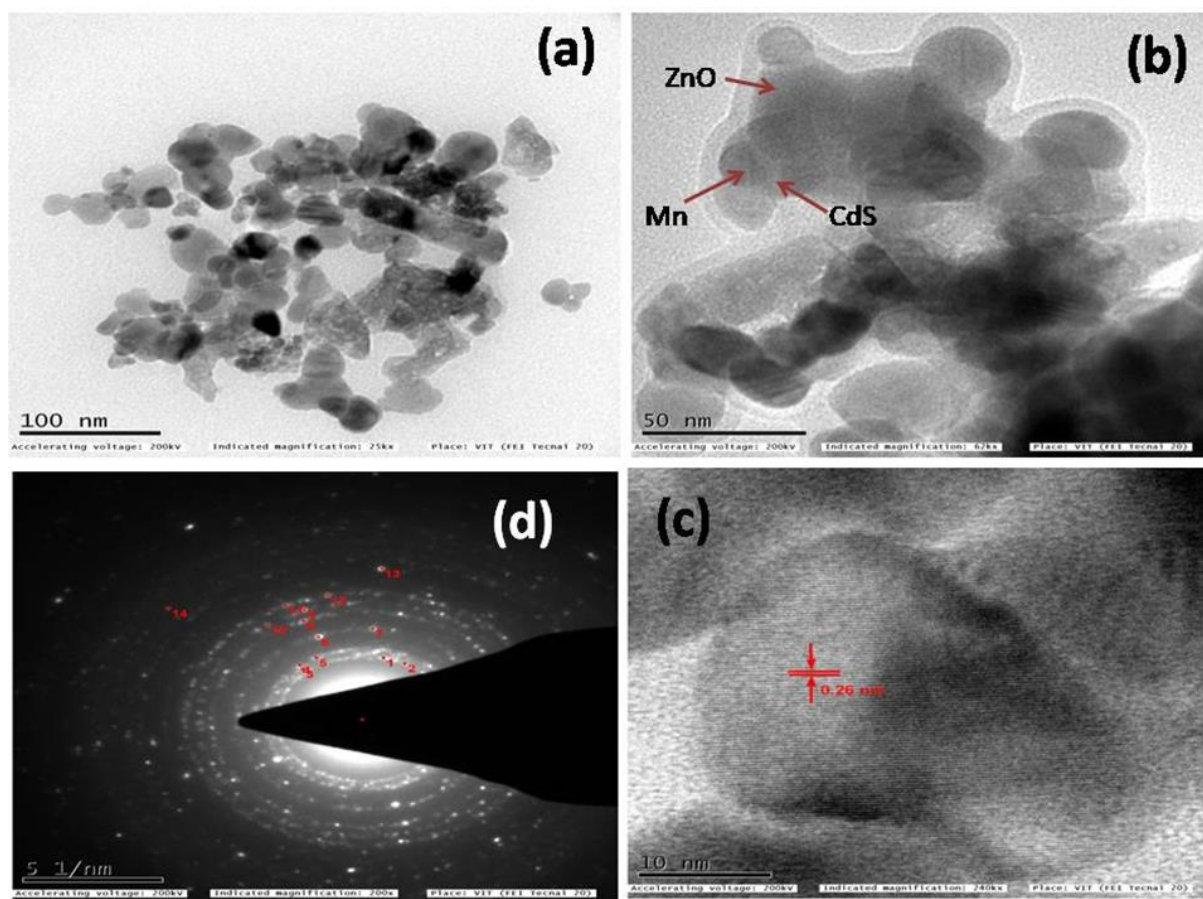


Fig. 4. (a) 100 nm (b) 50 nm and (c) 10 nm views of TEM image of 0.8 mol% Mn doped CdS-ZnO nanocomposites and (d) selected area electron diffraction (SAED) pattern of Mn doped CdS/ZnO nanocomposites

Optical properties analysis

It is well known that the optical absorption properties of photocatalyst is an important factor in determining the photocatalytic performance since the formation of photogenerated electron-hole pairs and reactive species under light irradiation are the prerequisite for photocatalytic reaction.

UV–Vis diffused reflectance spectra of pure ZnO, pure CdS, 25 % CdS/ZnO, 0.2 mol% Mn doped CdS/ZnO, 0.4 mol% Mn doped CdS/ZnO and 0.8 mol% Mn doped CdS/ZnO nanocomposites are shown in Figure 5. From the DRS result the pure ZnO shows maximum absorbance only in the ultraviolet region not in the visible region and it agrees well with the pervious results [43,44]. The bare CdS shows an admirable visible light absorption in the DRS spectra.

Moreover, ZnO/CdS binary nanocomposite has intense UV absorbance upto 410 nm and moderate visible absorbance at 590 nm. Obviously, the expansion of the range of responsive light to visible light of the ZnO/CdS binary nanocomposite can be observed. This is due to the CdS cover over the ZnO surface. Further, the Mn doped CdS/ZnO nanocomposites show higher absorption in the visible light region compared with 25 % CdS/ZnO. Mn doped CdS/ZnO nanocomposites absorption band is extended to red region (bathochromic shift). The excellent band shift of Mn doped CdS/ZnO nanocomposites is due to Mn ions located inertial position or crystal lattice of CdS/ZnO. From the absorption results of Mn doped CdS/ZnO, both Mn and CdS may decrease the electron-hole recombination and increase the visible light absorption. This enhancement property is beneficial for photocatalytic dye degradation processes.

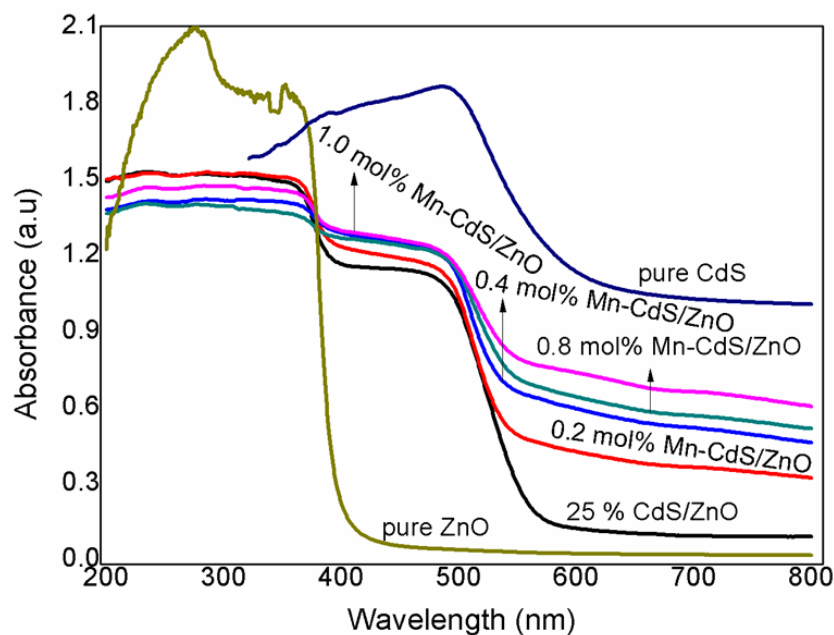


Fig. 5. UV-visible DRS spectra of pure ZnO, CdS, 25 % CdS/ZnO binary composites, 0.2 mol% Mn doped CdS/ZnO, 0.6 mol% Mn doped CdS/ZnO and 1.0 mol% Mn doped CdS/ZnO nanocomposites

The band gap of photocatalyst samples was estimated by Kubelka Munk function. The calculated band gap of ZnO, 25% CdS/ZnO and 0.8 mol% Mn doped CdS/ZnO nanocomposites are 3.18, 2.86 and 2.54 eV respectively. The band gap of CdS/ZnO binary nanocomposites is decreased than the parent ZnO, due to the CdS cover with ZnO. When Mn ion is doped on the CdS/ZnO matrix, decreasing the band gap (2.54 eV) reveals that Mn ion has changed the band structure of CdS/ZnO binary nanocomposites.

Electron-hole recombinations analysis

Photogenerated electron-hole pair's separation rate was analyzed by photoluminescence spectra. Lower PL intensity indicates the superior electron-hole separation rate. In other words the intense PL peak explains larger electron-hole recombination rate [45]. **Figure 6** indicates PL spectra of ZnO, 25 % CdS/ZnO, 0.2 Mn doped CdS/ZnO, 0.4 Mn doped CdS/ZnO and 0.8 Mn doped CdS/ZnO nanocomposites. All the samples give their own characteristic emissions peak of ZnO due to the vacancies in the surface or lattice of ZnO. When CdS is fabricated into the ZnO surface the band intensity is much weakened. The lower intensity of CdS/ZnO binary composites clearly represents the inhibition of electron hole recombinations.

The peak intensity of the Mn doped CdS/ZnO nanocomposites shows much lower than that of the ZnO and 25 % CdS/ZnO binary composites. It indicates that the composition of the Mn doped CdS/ZnO binary composites effectively inhibits the recombination of photogenerated carriers. Therefore, photogenic carriers can be better used in photocatalytic redox process and make their good photocatalytic properties to promote the degradation reactions.

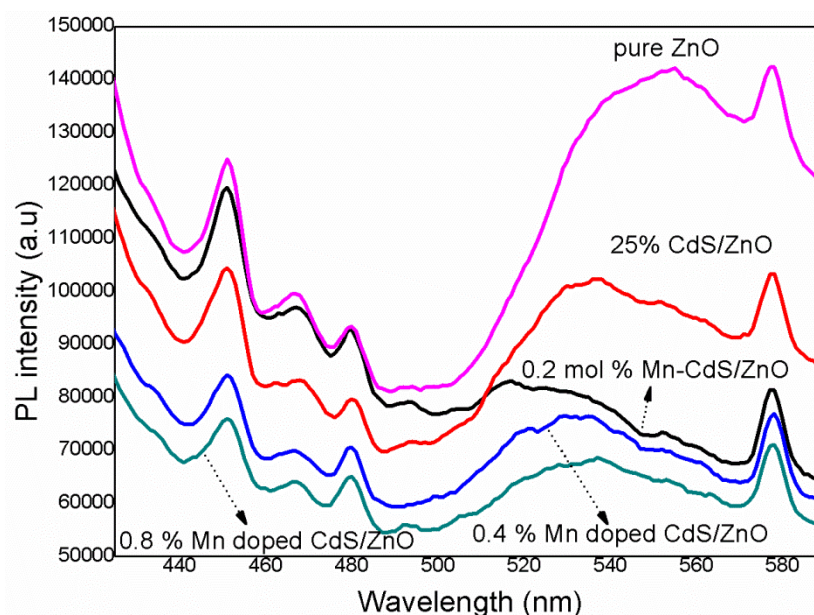


Fig. 6. PL emission spectra of pure ZnO, 25 % CdS/ZnO binary composites, 0.2 mol% Mn doped CdS/ZnO, 0.4 mol% Mn doped CdS/ZnO and 0.8 mol% Mn doped CdS/ZnO nanocomposites

The formation of large amount of photogenerated carriers could be induced the production of radicals to degrade the organic pollutants.

Photocatalytic studies

The semiconductor photocatalysis mainly focuses on generation photoelectron-holes for the degradation of organic pollutants in the way of production of effective radicals. Thus, the photocatalytic activity of semiconductor photocatalysts depend on its better morphology, good optical response, large surface area, small particle size, good crystallinity and large amount of surface hydroxyl ions. If the external surface is provided for the charge carriers, they will relocate where the electrons are caught by the semiconductor while the holes are trapped by hydroxyl

radicals and form $\text{OH}^\bullet$ and $\text{HO}_2^\bullet$. The transition metal doped hybrids are largely produce hydroxyl radical and these radicals effectively degrade methylene blue dye [46].

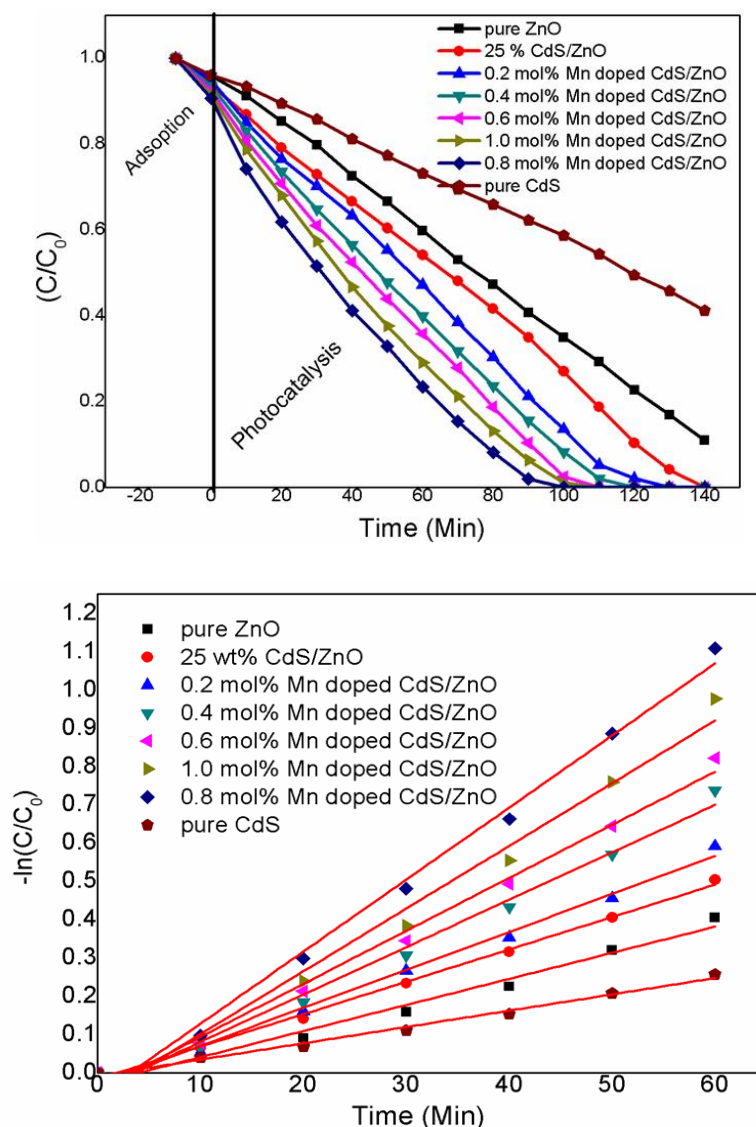


Fig. 7. Photocatalytic degradation and kinetics of pure ZnO, CdS, 25 % CdS/ZnO binary composites, 0.2 mol% Mn doped CdS/ZnO, 0.8 mol% Mn doped CdS/ZnO and 1.0 mol% Mn doped CdS/ZnO nanocomposites

The photocatalytic degradation and adsorption performance of ZnO, CdS, 25% CdS/ZnO, 0.2 mol% Mn doped CdS/ZnO, 0.4 mol% Mn doped CdS/ZnO, 0.6 mol% Mn doped CdS/ZnO, 0.8 mol% Mn doped CdS/ZnO and 1.0 mol% Mn doped CdS/ZnO nanocomposites were investigated, as shown in Fig. 7. The photolysis parameter is not beneficial for degradation of MB dyes even though there is a continuous irradiation of light. Before starting photocatalytic experiment, the suspension (photocatalytic mixture) was stirred for 30 min to reach the equilibrium adsorption and desorption to evaluate the adsorption performance of these samples. The results show that the adsorption rate of ZnO, CdS, 25% CdS/ZnO, 0.2 mol% Mn doped CdS/ZnO, 0.4 mol% Mn doped CdS/ZnO, 0.6 mol% Mn doped CdS/ZnO, 0.8 mol% Mn doped CdS/ZnO and 1.0 mol% Mn doped

CdS/ZnO nanocomposites for MB were 4.03%, 3.21%, 6.25%, 5.10%, 6.44%, 8.50%, 9.27% and 7.5% respectively, implying that the adsorption ability of all these materials is very weak.

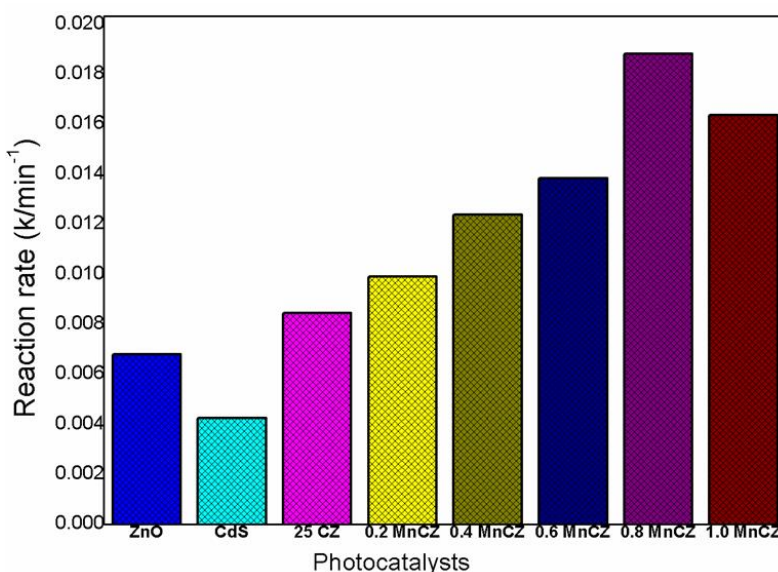


Fig. 8. Bar graph of pure ZnO, CdS, 25 % CdS/ZnO binary composites, 0.2 mol% Mn doped CdS/ZnO, 0.8 mol% Mn doped CdS/ZnO and 1.0 mol% Mn doped CdS/ZnO nanocomposites

The pure ZnO photocatalyst exhibited lower degradation results because of their wide band gap and no capability of absorption of visible light. Conversely, the CdS/ZnO binary nanocomposites show energetic degradation efficiency than the parent ZnO because of CdS inject its photogenerated electrons to the ZnO and the absorbance band shifted to red region, which resulted in the absorption of visible light.

Further, the photodegradation activities of CdS/ZnO binary nanocomposite with different mole ratio of Mn content were examined using methylene blue under solar light irradiation. All the Mn doped CdS/ZnO nanocomposites show good photocatalytic activity. The better performance of Mn doped CdS/ZnO nanocomposites coincide with above mentioned basic characteristics (proved by physicochemical characterization techniques) of semiconductor photocatalysts. Among the Mn doped CdS/ZnO nanocomposites, 0.8 mol % Mn doped CdS/ZnO nanocomposite shows better dye degradation efficiency. The main reason was 0.8 mol% of Mn content has sufficiently produced super oxide ion radical and hydroxyl radical in the way of effective photogenerated electron hole charge separation mechanism [47]. This enhanced photocatalytic efficiency achieved by within the 110 minutes. The 0.2 mol % Mn doped CdS/ZnO nanocomposites showed lowest activity due to very little amount of Mn doped on CdS/ZnO binary nanocomposites. In addition, when the Mn content increases beyond the optimum level of 0.8 mol%, it decreases the catalytic activity [48]. The excess transition metal gets agglomeration due to overlapping and forms a cluster. The cluster surface (agglomeration) formation is due to diminished rate of charge separation as well as photocatalytic activity [49,50].

The data obtained from the degradation studies were analysed with the Langmuir–Hinshelwood kinetic model. From the degradation rate data, which denotes the pseudo first order kinetics which is shown in Figure 8 and their rate constant values are given in the Table 1. The

Table shows the reaction rate constant of 0.8 mol% Mn doped CdS/ZnO composite is $0.0188 \text{ k/min}^{-1}$, which is one time of CdS/ZnO binary composites and three times of bare ZnO.

The photocatalytic degradation ability of CdS was also tested using MB dye. Its activity was very low compared to all the photocatalyst samples even though it has good band structure. This shows that the CdS has a smaller electron-hole diffusion length than ZnO which leads to the recombination of most of the photogenerated electron-hole pairs inside the CdS particle before reaching its surface.

Table 1. Kinetic plot of degradation of reactive blue 160

S.No	Photocatalysts	k/min^{-1}	R^2
1	ZnO	0.0068	0.9816
2	CdS	0.0043	0.9916
3	25% CdS/ZnO binary composites	0.00846	0.9968
4	0.2 mol % Mn doped CdS/ZnO	0.0099	0.9919
5	0.4 mol % Mn doped CdS/ZnO	0.0123	0.9882
6	0.6 mol % Mn doped CdS/ZnO	0.0130	0.9910
7	0.8 mol % Mn doped CdS/ZnO	0.0188	0.9920
8	1.0 mol % Mn doped CdS/ZnO	0.0163	0.9851

(dye concentration = 30 mg/L; catalyst dosage = 30 mg; pH = 5; time = 60 min; k/min^{-1} = reaction rate)

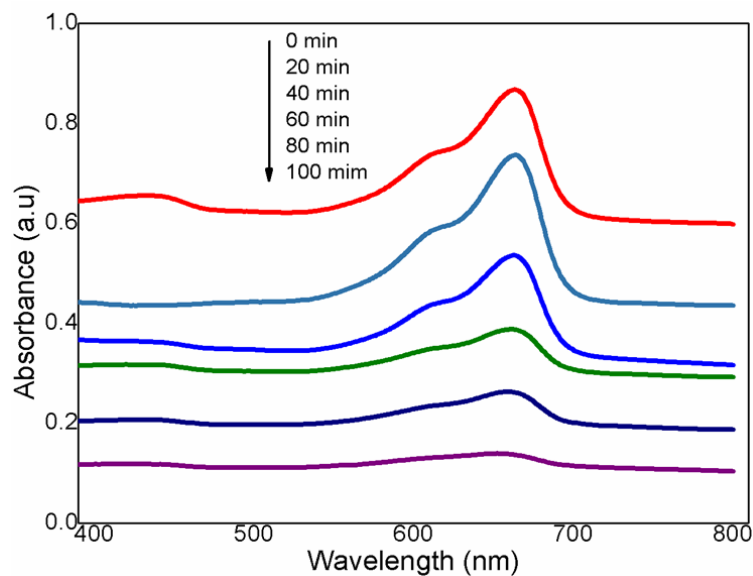


Fig. 9. UV-visible absorbance spectra presented the concentration of MB aqueous solution in the presence of 0.8 mol % Mn doped CdS/ZnO nanocomposites

The photocatalytic degradation process was further verified for the optimum photocatalyst like 0.8 mol % Mn doped CdS/ZnO nanocomposites over methylene dye solution. Figure 9 shows the degradation processes for 0.8 mol % Mn doped CdS/ZnO nanocomposites that were monitored by UV-visible spectrometer. As depicted, the absorption peak of MB at 664 nm is decreased gradually and the absorption intensity of MB for Mn doped CdS/ZnO significantly decreased by extension

of the exposure time. Generally, the absorbance of dye solution will be directly proportional to dye concentration. So that, decreasing the peak intensity of representative wavelength which indicates the decreasing concentration in the way of dye degradation.

A comparison of the outstanding photocatalytic degradation efficacy of the ZnO photocatalyst for the photodegradation of methylene blue dye (MB) with formerly reported ZnO-based photosystems is compiled in Table 2. It was distinctly noticed that the ZnO photocatalyst in the current study exhibited superior photodegradation efficiency compared to the previously reported catalysts.

Table 2. Comparative data of photocatalytic degradation of methylene blue dye using ZnO based nanoparticlebased photocatalysts under sunlight

S.No	Catalyst	Concentration	Catalyst Amount	Time (min)	Degradation (%)	Ref
1	Cellulose acetate/ZnO	5 ppm	20 mg	120	75	50
2	Polyaniline/Zinc oxide	1×10^{-5} M	0.4 mg/mL	300	97	51
3	ZnO nanorod	10 ppm	NA	150	100	52
4	Fe-Co-ZnO	5 ppm	30 mg	60	98.8	53
5	Mn doped CdS/ZnO nanocomposites	30 ppm	30mg	120	100	Herin

Reaction mechanism

A plausible mechanism was applied for the enhanced photocatalytic activity of Mn doped CdS/ZnO nanocomposites under solar light irradiation which is shown in **Figure 10**.

The enhanced photocatalytic activity of CdS/ZnO was significantly influenced by transition metal incorporate ion. Mn doped CdS/ZnO nanocomposites photodegradation efficiency is increased under the solar light radiation which is because of synergistic effect of Mn and CdS on ZnO surface. When irradiation of light falls on the CdS surface, the electron is excited from valence band (VB) to conduction band (CB). Further the ZnO also absorbs the light and does the same phenomenon of CdS. The conduction band of CdS was higher than the conduction band of ZnO. So that the photogenerated electron migrates to CB of CdS to ZnO CB, in addition with the hole moving from VB of ZnO to VB of CdS. This is due to lowest energy state.

Furthermore, the CB of ZnO and CdS was slightly decreased by the doping of Mn ion. From the band gap tuning process, the photoinduced electrons can be easily abstracted by O_2 which are converted as active species like super oxide ion radical (O_2^{2-}). The photogenerated hole attracts with the H_2O molecule to produce highly active hydroxyl radical (OH). Hence, the both OH and O_2^{2-} effectively bombarded the methylene blue structure and finally give mineralized products [39].

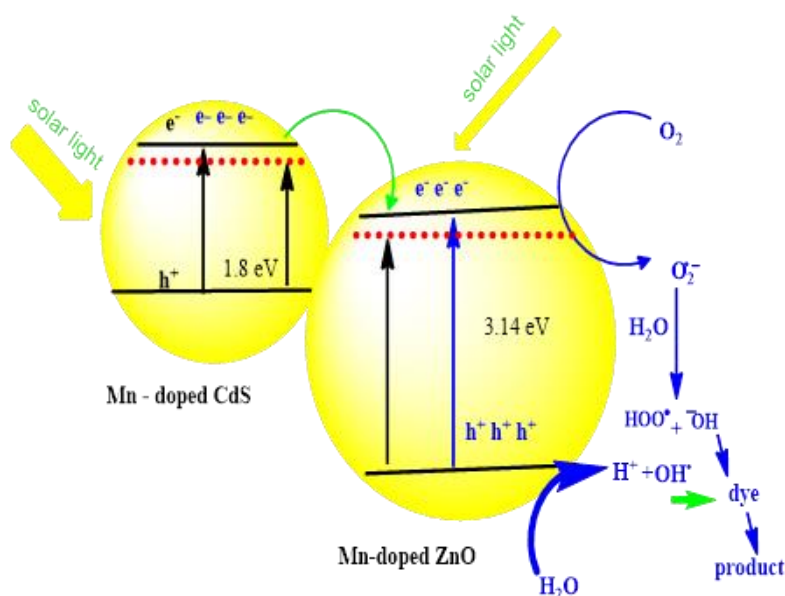


Fig. 10. Photocatalytic degradation mechanism of Mn doped CdS/ZnO nanocomposites

Quenching experiment

A quenching experiment was carried out to identify the potential contribution of various active species involved in the photocatalytic degradation. The radical trapping experiments were carried out the degradation of the MB under solar light irradiation and the results are shown in Figure 11.

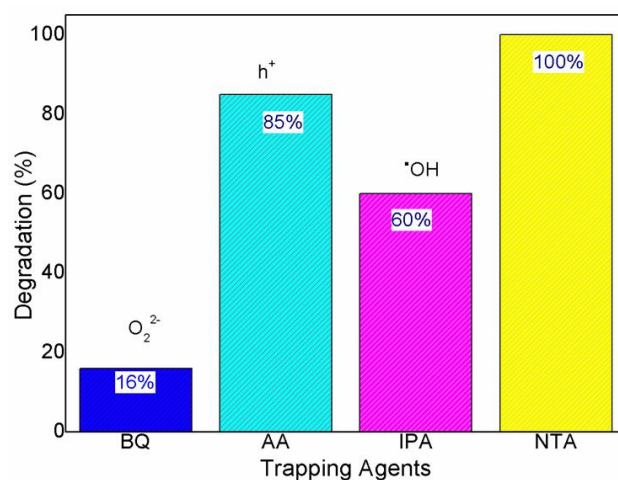


Fig. 11. Effect of different scavengers on degradation of MB in the presence of Mn doped CdS/ZnO nanocomposites

In order to detect (scavenging) the active species generated during the photocatalytic reaction, isopropanol (IPA, 5 ml) was used as $\bullet OH$ scavenger and benzoquinone (BQ, 2 mmol/L) for scavenging $O_2^{\bullet -}$. In addition, Ascorbic acid (AA, 0.2 g) was selected for scavenging hole (h^+) [51]. When BQ was added to the photocatalyst mixed composition, a dramatic change of reduction in the photocatalytic activity was observed compared to the absence of scavenger, confirming that the

dissolved oxygen (O_2^-), has a main source on the photodegradation process under sunlight irradiation.

However, an unusual photocatalytic activity change was also observed upon the addition of IPA as a OH scavengers. From the scavenging study it is found that the O_2^- and OH are the main reactive species in the Mn doped CdS/ZnO nanocomposites [47]. The degradation efficiency of Mn doped CdS/ZnO nanocomposites was decreased slightly in the presence of AA when compared with zero scavengers, which indicates the photogenerated holes are not the main active species for degradation of RO 30. As shown in the **Figure 11**, ~95% degradation of MB was found in the absence of any scavenger, while 16% degradation was found with BQ, 65 % with IPA and 85% with AA respectively.

Thus the order of reactive species involving in the photocatalytic degradation was superoxide anion radical > Hydroxyl radical > holes

Reusability and stability of the Mn doped CdS/ZnO nanocomposites

The evaluation of photostability and durability of the photocatalyst under repetitive photocatalytic cycle is essential for practical applications [52-54]. Recyclability of Mn doped CdS/ZnO nanocomposites was examined for five consecutive cyclic runs were shown in **Fig. 12**. After each cycle, the nanocomposites were taken off from the degraded MB dye solution and separated through ultra-centrifugation. This nanocomposite catalyst washed thoroughly with distilled water followed by drying at 100 °C and then transferred to a fresh MB solution. It can be seen that the photocatalytic activity of the Mn doped CdS/ZnO nanocomposites was decreased slightly to 2.2 % after four successive cycles due to adsorption of intermediate products on the photocatalyst active sites. It was observed that the photocatalytic degradation of MB dye were 100%, 100%, 100%, 100% and 97.8% for first, second, third, fourth and fifth cycles respectively. This indicates the good stability of Mn doped CdS/ZnO nanocomposites and could be potentially applied in the practical batch degradation. However, the prepared Mn doped CdS/ZnO nanocomposites has considerable stability under solar light irradiation.

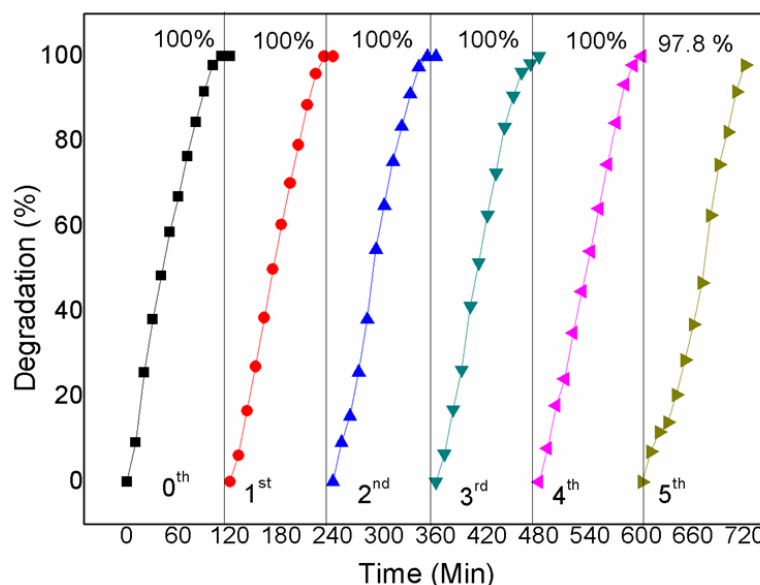


Fig. 12. Photostability test of Mn doped CdS/ZnO nanocomposites for fifth cycles

CONCLUSIONS

In summary, the Mn doped CdS/ZnO nanocomposites with different molar ratio of Mn to CdS/ZnO binary composites were successfully prepared by polar solvent assisted chemical coprecipitation method. The crystalline phase and structure of Mn doped CdS/ZnO nanocomposites were proved by XRD, techniques. The morphology and distribution of elements were characterized by TEM, FESEM and EDX. Furthermore, the PL study shows that the obtained Mn doped CdS/ZnO photocatalysts have a low intensity peak. Such result may favor the capture of photoinduced electrons and inhibit charge carriers recombination. The experimental results of the UV-DRS and the photodegradation demonstrated that Mn doped CdS/ZnO nanocomposites could absorb visible light (> 400 nm) and the enhanced photocatalytic ability under visible light irradiation. In addition, it exists in an optimal 0.8% molar ratio of Mn with the highest photocatalytic ability under solar light. In photostability experiments, dropping was only 2.2 % in the activity under the optimum conditions after four cycles. It showed Mn doped CdS/ZnO nanocomposites photocatalysts have high stability.

In addition, the mechanism of enhanced photocatalytic ability was found by active species quenching test. It was found that the deactivation sequence is as $BQ > IPA > AO$, indicating that the roles of $\cdot O_2^-$ and $\cdot OH$ in the photocatalyst reaction is much higher than that of h^+ . The radical scavenging measurement indicates that $\cdot O_2^-$ and $\cdot OH$ radicals play a crucial role in photocatalytic reaction. It is benefited from the existence of Mn and CdS/ZnO binary composites not only in promoting the charge separation and inhibits the fast charge recombination but also in improving photocatalytic oxidation performance. Hence, the results suggest that the Mn doped CdS/ZnO nanocomposites photocatalysts may have practical applications in photocatalytic dye degradation.

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Conflicts of interest

The authors hereby declare that there is no conflict of interest and satisfy all ethics in publishing policy.

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