


A Facile Platform for Photocatalytic Reduction of Methylene Blue Dye By CdSe-TiO₂ Nanoparticles

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Abstract Herein, we report on the demonstration of enhanced photocatalytic reduction of methylene blue (MB) dye using a physical mixture (*w/w* ratio: 50:1–9) of TiO₂ nanoparticles (size $\approx 20 \pm 1$ nm) and CdSe nanocrystals (size $\approx 3.0 \pm 0.2$ nm). It was found that at the highest content of the nanocrystals (9 mg) in the physical mixture, 67% reduction in the dye concentration could be achieved in a period of 60 min to prepare a physical mixture. Nanocatalyst characterization was accomplished using XRD, SEM, FTIR, UV-visible and Raman spectroscopy. The results showed that the prepared nanocatalyst could remove MB dye from waste water under the presence, as well as in the absence of UV- irradiation, while pristine TiO₂ nanoparticles or the CdSe nanocrystals did not possess sufficient photocatalytic activity in the absence of UV-radiation. It is concluded that presence of CdSe nanocrystals at a mass concentration of less than 5% can be used for the remediation of water polluted with industrial dyes.

Keywords Titanium dioxide · Cadmium selenide · Nano-catalyst · Photo-catalysis · Dye reduction · Water remediation

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Introduction

Nanomaterials possess remarkable physicochemical properties due to which they have received much attention from researchers from different areas of science and engineering, including bioremediation. Bioremediation allows a fairly good clean-up protocol for non-toxic treatment of certain types of waste. However, it does not provide solutions for all waste management situations. Bioremediation cannot always offer a feasible strategy at sites infested with high concentration of toxic chemicals and other pollutants, which may include heavy metals, dyes and phenolic compounds. Furthermore, the advancement in science and technology has increased standard of living which directly or indirectly contributes to the increase in waste and toxic material. Therefore, the remediation of contaminants by use of existing technology is often not effective and efficient in cleaning up the environment. In this paper, we have used a physical mixture of two nanomaterials (TiO₂ and CdSe) that have been individually used so far in bioremediation of waste water containing organic dyes [1].

Several studies have reported on the photocatalytic degradation of chemicals like organic compounds (2-chlorophenol, 4-chlorophenol) using TiO₂ nanoparticles [2] and CdS-sensitized TiO₂ [3]. The photo-assisted oxidation of pentachlorophenol in TiO₂ nanoparticle suspension has been investigated [4]. An extensive investigation performed on photocatalytic degradation of pentachlorophenol in aqueous solution utilizing immobilized TiO₂ has been reported [5, 6]. Recent investigations have shown the effect of transition metal ions doped in TiO₂ on the photo-degradation of 4-nitrophenol. Wolf et al. have observed improvement in W⁵⁺-TiO₂ nanoparticle system in the photocatalytic degradation of 1, 4-dichlorophenol [7].

Apart from TiO₂ nanoparticles (NPs), bismuth silicates under xenon lamp irradiation have successfully been used to degrade the pentachlorophenol largely mediated by superoxide radical (O₂⁻) [8]. Incorporation of transition metal ions into TiO₂ is known to enhance the lifetime of photo-generated oxidation and reduction equivalents. It has been conceptualized that transition metal ions incorporated in semiconductor materials are oxidized and/or reduced by the conduction band electrons [9]. For instance, UV-irradiated TiO₂-Fe³⁺ nanoparticles enhanced the EPR signal [10]. In addition, Fe³⁺ and Cu²⁺ ions were found to inhibit electron-hole recombination [11], whereas Cr³⁺ increased the recombination process [12]. The aforesaid results motivated the present work which is aimed at the design of novel nanomaterials either through physical or chemical blending to propose a facile platform for water remediation.

Materials and Methods

Synthesis

Synthesis of CdSe The details of synthesis CdSe quantum dot (QD) at room temperature has been discussed elsewhere [13]. In the procedure of CdSe quantum dots synthesis, we prepared Cd stock solution and reacted it with NaHSe solution at room temperature (20 °C). In this procedure, 0.2012 g of CdCl₂·H₂O (20 mmol) was dissolved in 100 ml of deionized water, followed by the addition of 400 μl of 3-MPA. The pH of the solution was maintained at 11 by the addition of 1.0 M of NaOH solution. This solution was then reacted with NaHSe solution at room temperature. The later was prepared by reacting selenium (40 mmol/0.0632 g) with NaBH₄ (80 mmol/0.0636 g) under stirring for 1 h. This mixture was further stirred for 60 min, and a clear yellow CdSe dispersion was obtained.

Synthesis of TiO₂ TiO₂ nanoparticles were prepared by economical non-hydrolytic sol-gel route [14]. Ten millilitre of titanium tetra-isopropoxide (Spectrochem, India) was added to 40 ml of 2-methoxy ethanol (SRL Chemical, India) used as solvent and magnetically stirred at room temperature with addition of few drops of 1.0 M HNO₃ to maintain the pH value at 3. The solution was maintained under stirring which resulted in gel formation, which was dried under infrared lamp followed by pulverization to generate an amorphous powder. To obtain crystalline anatase phase, amorphous powder was calcined at 450 °C for 1 h under ambient condition.

Characterization

Information about the morphology, crystal structure and average particle size of CdSe and TiO₂ nanomaterial was obtained

from transmission electron microscope (TEM) images, taken at 200 kV (JEOL 2100F, field emission with magnification of 150,000×). The samples used for CdSe-TiO₂ TEM analysis were prepared as follows. A suitable amount of the nanomaterials of CdSe and TiO₂ were taken separately, and as a well mixture of the two was dispersed in a given volume of deionized water which was ultrasonicated at room temperature for 5 min. Then, a drop of the dispersion was spread over a 200 mesh copper grid with perforated carbon film and air dried at room temperature (20 °C) for 1 day.

Dynamic light scattering (DLS) experiments were conducted using a 256-channel digital correlator (Photocor Instruments, USA) used in the multi-τ mode (logarithmically spaced channels) at scattering angle of $\theta = 90^\circ$ and using a laser of wavelength of $\lambda = 632.8$ nm. The details of the instrument can be found elsewhere [15]. The correlator measures the intensity function $g_2(\tau)$ from which the relaxation time is deduced. The translational diffusion coefficient D , determined from the relaxation time, is related to apparent hydrodynamic radius R_h through the Stokes-Einstein relation given by

$$D = \frac{k_B T}{6\pi\eta_0 R_h} \quad (1)$$

where the solvent viscosity, absolute temperature and Boltzmann constant are given by η_0 , T and k_B , respectively.

Scanning electron microscopy (SEM) images were obtained using EVO, 40 ZEISS, SEM Instrument to analyse surface morphology. The compositions and purity of nanocrystals was determined from the energy dispersive analysis of X-rays (EDAX). UV-visible absorption spectra were recorded on UV-visible spectrophotometer (T90+ UV-visible spectrometer, UK). X-Ray diffraction (XRD) experiments were performed on a Rigaku D/Max 2200 diffractometer using CuK_α radiation ($\lambda = 1.5406$ Å). The details of the instrument can be found elsewhere [16].

Photocatalytic Activity

The photocatalytic activity of pristine TiO₂, CdSe and physical mixture of TiO₂-CdSe was spectroscopically analysed to note the degradation of methylene blue (MB) dye under UV light exposure. The reactions were carried out in a glass beaker containing 100 ml dye solution (10 ppm or 10 mg/L) and the required amount of nanomaterial. This aqueous suspension was kept under constant stirring and was irradiated with UV light of wavelength 254–365 nm (Osram ultra-vitalux, 300 W) for time duration of 150 mins. After regular time intervals of 15 mins, 3 ml of dye solution is withdrawn, and its concentration was measured by recording the absorbance corresponding to $\lambda \approx 664$ nm.

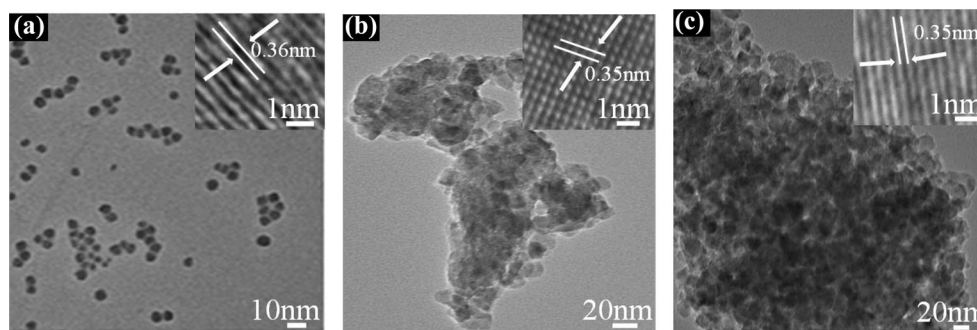


Fig. 1 TEM image of **a** CdSe QDs shows average size 3.0 ± 0.2 nm and inset HRTEM, **b** clusters TiO_2 with average size 20.0 ± 1.0 nm and inset HRTEM **c** physical mixture of CdSe and TiO_2 with inset HRTEM. Note

that TEM of CdSe- TiO_2 does not show the presence of CdSe because of large size of TiO_2 clusters

Results and Discussion

Morphology and Compositional Analysis

TEM results (Fig. 1) show that CdSe QDs (Fig. 1a) were of spherical nature with average size of 3.0 ± 0.2 nm, and it was 20.0 ± 1.0 nm for TiO_2 NPs (Fig. 1b). Figure 1c depicts the morphology of CdSe- TiO_2 clusters. The inter-planar distance obtained from TEM analysis was 3.8 \AA for CdSe, 4.0 \AA for TiO_2 and 4.0 \AA CdSe- TiO_2 mixtures. The particle size distribution was determined from TEM (Fig. 1) and DLS (Fig. 2) profiles. Hydrodynamic radius determined from DLS data (Fig. 2) gave us better information regarding the average cluster size in the solution. As shown in (Fig. 2a), $R_h = 14$ nm for CdSe QDs and $R_h = 210$ nm for TiO_2 NPs. Figure 2b depicts the characteristic absorption spectrum of the nanomaterials used (Table 1) for the study.

The morphologies and size of the as-synthesized products were examined by SEM. The SEM images (Figs. 3a, b) show that the as-synthesized product consists of spherical CdSe QDs, and flower-like TiO_2 nanoparticles, respectively. Figure 3a, b depicts planar SEM micrographs showing

relatively homogeneous and compact structure of the nanoparticles. The corresponding EDAX measurement (Fig. 3c, d) shows the major elemental compositions of CdSe were Cd and Se, and of TiO_2 were Ti and O. The chemical composition was estimated to be $\text{Cd}_{3.79}\text{Se}_{4.04}$ and Ti_8O_2 . In addition, the EDX results revealed that the chemical composition of the CdSe QDs is slightly decreased in content of Se compared to that of the original elemental ratio of CdSe_2 . It is to be noted that, qualitatively, EDX analysis confirmed the presence of constituent elements in CdSe and TiO_2 samples.

Optical Properties

UV-visible absorption spectroscopy is an extremely useful analytical tool for monitoring optical properties of nanocrystal. As a result of quantum confinement and band-edge energy in semiconductor nanocrystals, the first exciton peak detected by static absorption can be used to determine the band-edge energy. As shown (Fig. 2b), the first absorption peak for CdSe QDs was at $\lambda_{\text{max}} \approx 420$ nm and for TiO_2 , it was at 400 nm.

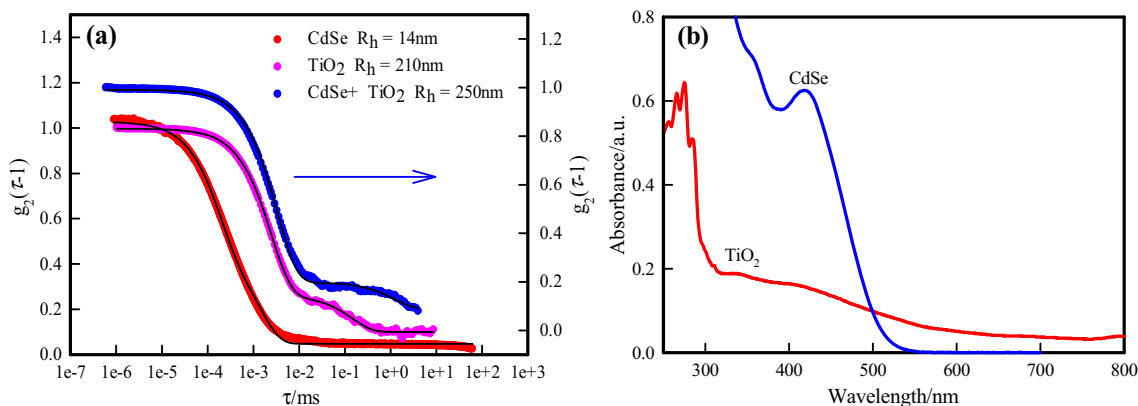


Fig. 2 **a** Hydrodynamic radius R_h of CdSe quantum dots ($R_h = 14$ nm), TiO_2 NPs ($R_h = 210$ nm) and CdSe- TiO_2 mixture ($R_h = 250$ nm) determined from the correlation function. **b** Absorption spectra of CdSe and TiO_2 nanocrystals. Note CdSe- TiO_2 mixture had the same absorbance spectra as that of TiO_2

Table 1 Comparison of physical properties of CdSe nanocrystals and TiO₂ nanoparticles

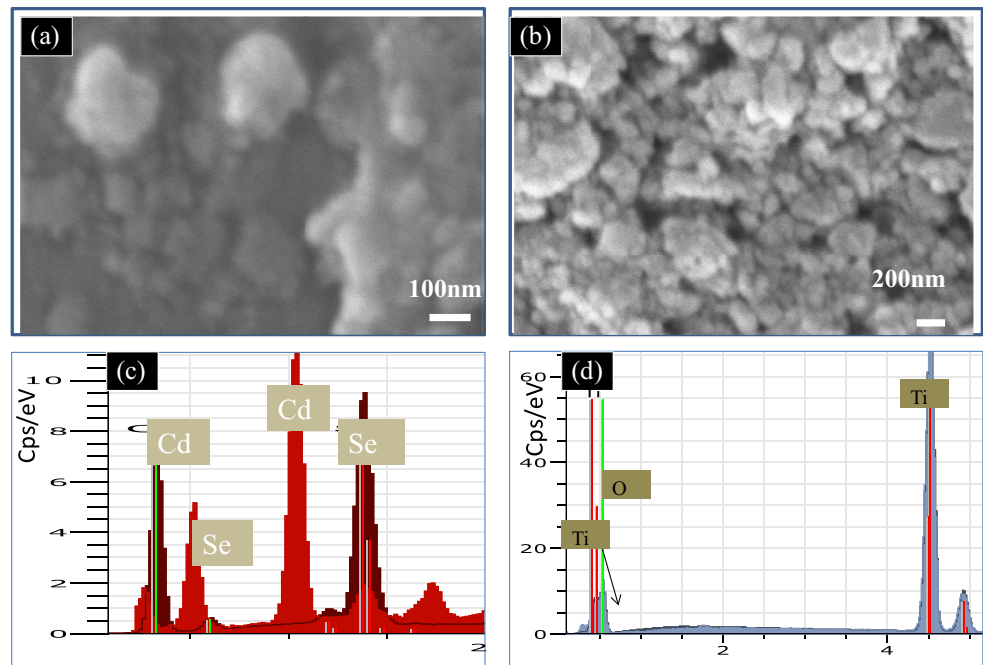
Parameter	TiO ₂	CdSe	Mixture
Average core size/nm (TEM)	15	3.0	15
Cluster size/nm (DLS)	210	14	250
EDX composition (% atomic weight)	Ti ₈ O ₂	Cd _{3.79} Se _{4.04}	Ti ₇ O ₂
Absorption peak (λ_{\max})/nm	400	420	400

Crystalline Structure

The XRD pattern (Fig. 4) of CdSe was considerably broadened due to very small size of the QDs. Pure anatase phase of TiO₂ nanoparticles was confirmed with tetragonal symmetry. The XRD pattern exhibited prominent broad peaks at 2θ values of 25.2°, 42.2° and 49.4° for CdSe, and 25.5°, 38.05°, 48.20°, 54.16°, 55.30°, 62.90°, 69.03°, 70.46°, 75.22° and 80.08° for TiO₂ which were identified for cubic CdSe phase and tetragonal TiO₂ phase. The respective dominant peaks represent reflections originating from (111), (220) and (311) planes for CdSe QDs and (101), (004), (105), (211), (204), (116), (220) and (110) for TiO₂ nanoparticles, which is in agreement with JCPDS File No: 32-0483 [17]. The most intense peak at $2\theta = 25.2^\circ$ corresponding to (111) and at $2\theta = 25.5^\circ$ corresponding to (101) reflections (for CdSe and TiO₂, respectively) was observed from the X-ray diffractogram, thus indicating preferred orientation along this direction. Using the Debye-Scherrer formula, the average crystallite size (D_x) was calculated.

$$D_x = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

Fig. 3 SEM image of **a** CdSe QDs and **b** TiO₂ nanoparticles shows clusters of CdSe and TiO₂. EDAX plot of **c** CdSe QDs and **d** TiO₂ nanomaterials showing the purity of the sample



where β is the full-width at half maximum (FWHM), K is a constant known as the shape factor taken as 0.89 because of spherical shape of NPs, θ is the diffraction angle and λ is the wavelength of X-ray radiation.

From the diffraction data, it was found that the QDs had crystallite size of 3.0 nm, and these belong to the fcc phase with orientation in the (111) direction. Also, the crystallite size for pristine TiO₂ nanoparticle was 15 ± 2.0 nm corresponding to the tetragonal phase. XRD pattern did not show any additional peaks indicating the formation of pure and single phase. The calculated inter planar spacing determined from the reflection peak (111) was 3.53 and 3.49 Å for CdSe nanocrystals and TiO₂ nanoparticles, respectively. We found that TiO₂ and CdSe-TiO₂ showed same crystal structure because of two reasons: (i) in the mixture, we have very low concentration of CdSe (3% only) and (ii) TiO₂ showed very high diffraction intensity compared to CdSe (Table 2).

Photocatalytic Degradation of MB Dye

The photocatalytic degradation of MB dye under UV irradiation without any catalyst showed absorption peak at 664 nm. Figure 5a shows absorption spectra of UV irradiation (for 150 min) for different prepared compositions of CdSe and TiO₂. Clearly, we observe a significant decrease in absorbance intensity of MB in the presence of mixture of CdSe and TiO₂ compared to individual constituents. It was found that 65% MB dye degraded within 150 min in the presence of mixture (50 mg TiO₂ + 9 mg CdSe) which is higher than that obtained from presence of CdSe QDs (10%) and TiO₂ nanoparticles (48%). This suggests

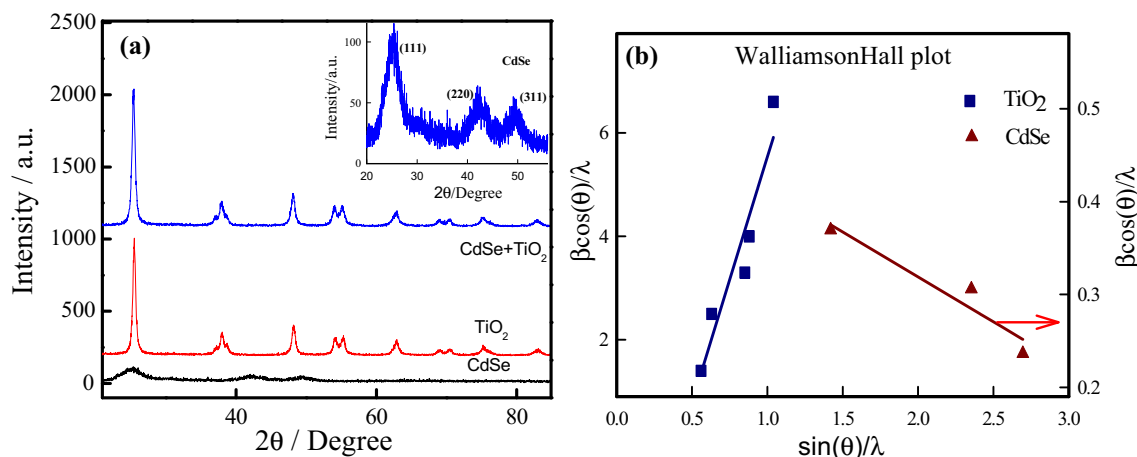


Fig. 4 **a** X-ray diffraction patterns of CdSe, TiO₂ and CdSe-TiO₂ (mixture) samples. From the analysis, we found the inter-planer spacing, $d = 3.53$ and 3.49 \AA , respectively for CdSe and TiO₂. Inset shows XRD pattern of CdSe. Note that there is no apparent change in

crystal structure of CdSe-TiO₂ (mixture), it is identical to TiO₂. **b** Williamson-Hall plot gives more accurate average crystallite size, as $D_x = 3 \text{ nm}$ for CdSe and 20 nm for TiO₂ and the CdSe-TiO₂ mixture

CdSe-TiO₂ blend was a more efficient catalyst for degradation of dye. In addition to this, we observed blue shift in maximum absorption wavelength of MB solution which increased with mass fraction of CdSe quantum dots in the mixture. This could be attributed to reduced absorbance value of the decomposed products. Figure 5b shows plot of normalized concentration with time at maximum absorption wavelength for variable compositions of the mixture. This plot can be used to calculate rate constant (k , rate of degradation of dye), because photo-degradation process was fitted to pseudo first-order kinetics using the formula

$$k = \frac{\left\{ \ln \left(\frac{C_0}{C} \right) \right\}}{t} \quad (3)$$

where C_0 is the maximum absorbance at time $t = 0$ and C is the absorbance at time t .

Figure 6 shows the plot of rate constant k as a function of % amount of CdSe quantum dots in the physical mixture of TiO₂ nanopowder and CdSe quantum dots. The percentage amount of CdSe was calculated from

$$\% \text{ amount of CdSe} = \frac{\text{Amount of CdSe}}{\text{Amount of TiO}_2 \text{ nano-powder} + \text{Amount of CdSe}}$$

We found that 5.66% amount of CdSe with TiO₂ gives a maximum rate constant k value of $3.97 \times 10^{-3} \text{ min}^{-1}$. The above results showed that increasing the amount of CdSe quantum dots had a direct and remarkable influence on the photocatalytic activity of TiO₂ nanoparticles.

Coupling TiO₂ with small band gap semiconductors has proven to be a milestone for improvement in photocatalytic activity. High density single crystalline TiO₂/CdSe nanowires has been successfully grown on Ti substrate by chemical

Table 2 Different parameters calculated from XRD data of CdSe QDs and TiO₂ nanoparticles. Note that CdSe-TiO₂ mixture had parameters similar to that of TiO₂

	Planes (hkl)	2θ (degree)	FWHM (degree)	Crystallite size (nm)	Parameters from William-Hall plot		
					Strain $\times 10^{-3}$	Density dislocation $\times 10^{16}$ lines/m ²	Crystallite size (nm) W-H plot
CdSe	(111)	25.20	3.84	2.10	-24.19	25.00	3.02
	(220)	42.20	4.36	1.94			
	(311)	49.40	4.39	2.02			
TiO ₂	(101)	25.51	0.51	16.0	23.93	0.25	20.1
	(200)	48.23	0.60	14.1			
	(204)	62.85	0.88	11.2			
	(215)	75.34	0.99	10.2			
	(224)	82.97	1.24	8.57			

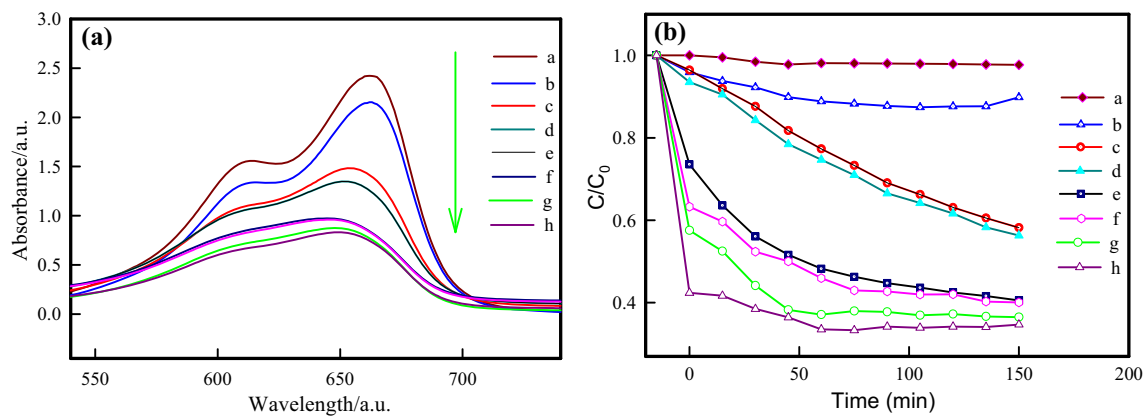


Fig. 5 **a** Absorbance spectra of MB solution after 150 min of UV irradiation and **b** normalized concentration plot with time for **a** without any catalyst; with **b** 5 mg CdSe; **c** 50 mg TiO₂; **d** 50 mg TiO₂ + 1 mg

CdSe; **e** 50 mg TiO₂ + 3 mg CdSe; **f** 50 mg TiO₂ + 5 mg CdSe; **g** 50 mg TiO₂ + 7 mg CdSe and **h** 50 mg TiO₂ + 9 mg CdSe. All measurements were done at room temperature (20 °C)

vapour deposition [18]. These nanowires were found to degrade MB dye completely within 80 min of UV irradiation. Cardiel et al. reported [19] TiO₂-WO₃ composite for MB dye degradation with highest k value of $2.7 \times 10^{-3} \text{ min}^{-1}$ was achieved, which was found to be less than our reported k value of $3.97 \times 10^{-3} \text{ min}^{-1}$. CdS and CdSe nanoparticle deposited on ordered TiO₂ nanotubes [20] were found to efficiently degrade methylene orange dye (up to 95%) within 120 min of visible light irradiation. Ninety percent MB dye degradation was achieved in the presence of visible light by TiO₂/CuS composite nanostructure, synthesized via surface functionalization route [21]. In all the above-mentioned reports, there was a requirement of integrating TiO₂ with semiconductors into a single nanoscale heterostructure, which in itself requires extensive synthesis. But our method avoids this step and shows that a physical blend of TiO₂ with CdSe can efficiently degrade the organic pollutant present commonly in effluents from textile industries.

Photo-Catalytic Activity and Mechanism

The photocatalytic activity of TiO₂ arises due to production of electron-hole pair by absorbing energy either greater than

or equal to energy gap. The electron being produced is promoted to conduction band, and hole remains in valence band. These electron hole pair may recombine or dissipate some energy to reach metastable states. The electron in metastable state interacts with oxygen vacancies to generate superoxide ions, whereas the hole (in the metastable state) interacts with adsorbed H₂O or OH⁻ ions at the catalyst-water interface to form highly reactive hydroxyl radicals. These highly active oxygen species oxidize organic pollutants into simple CO₂ and H₂O molecules. To enhance photocatalytic activity of TiO₂ significant amounts of dopants were used in recent years. Further each one required UV or visible light irradiation for activation. It would be interesting to explore the efficacy of modified TiO₂ nanostructure that does not require any light.

It was found that all CdSe-TiO₂ samples exhibited enhanced photo-degradation activity compared to bare TiO₂ nanoparticles. This accounts for photocatalytic activation of CdSe QDs. In the absence of light, thermally generated electrons in conduction band of CdSe may tunnel to conduction band of TiO₂ and react with O₂ to form reactive oxygen-species (ROS), whose number increase with CdSe content,

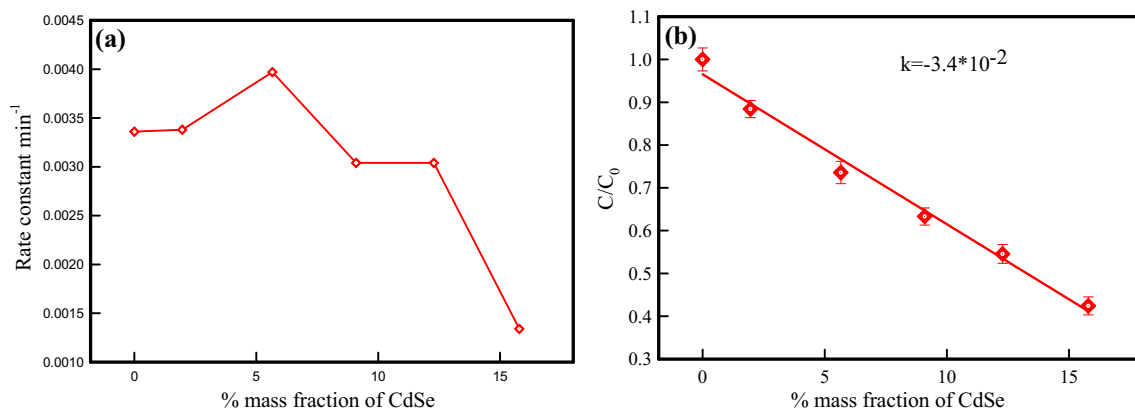
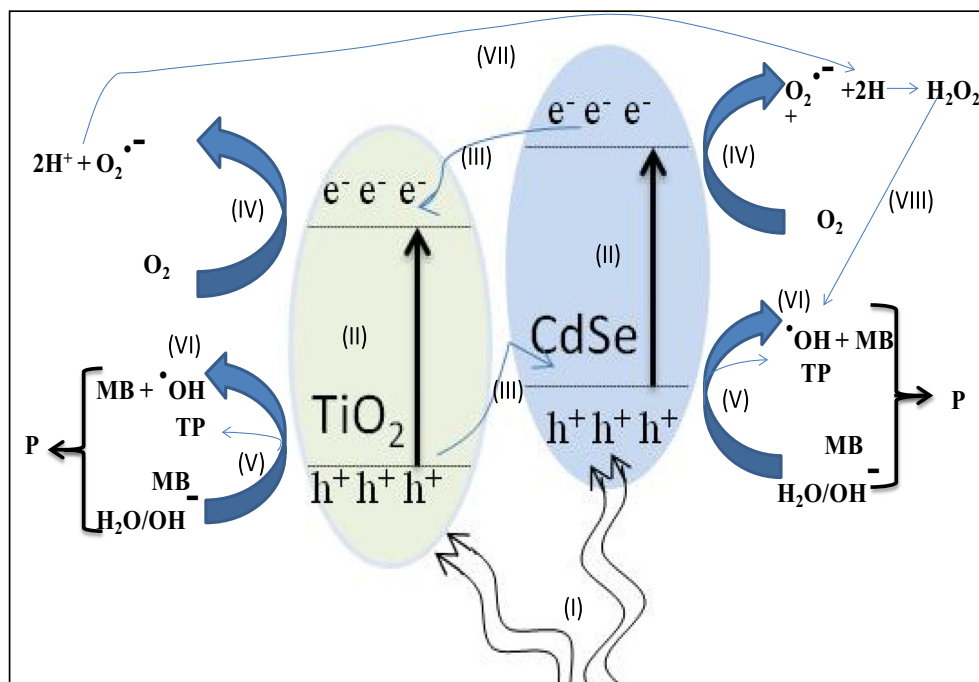


Fig. 6 **a** Rate constant, k as function of percentage mass fraction of CdSe quantum dot in physical mixture of TiO₂ and CdSe. **b** Normalized concentration without using any source of illumination with percentage mass fraction of CdSe quantum dot in physical mixture of TiO₂ and CdSe

Fig. 7 Schematic diagram of the photocatalytic reaction of MB on TiO₂/CdSe



and therefore may be responsible for enhanced degradation efficiency.

It is widely accepted that generation and separation of electron-hole pairs is necessary for the photocatalytic action of semiconductors [22]. The proposed mechanism of MB dye degradation by the nanocomposite photocatalyst is discussed in numbered steps in Fig. 7. When TiO₂ is irradiated with light of energy equal to or greater than the Fermi gap energy, an electron-hole pair is produced on the surface of TiO₂. When the nanocomposite system is illuminated (I in Fig. 7) with the UV light, both TiO₂ and CdSe are activated and generate e⁻ and h⁺ in their respective conduction and valence bands (II in Fig. 7).

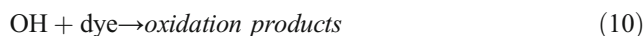
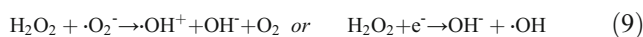
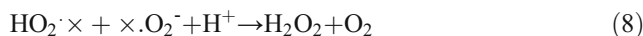
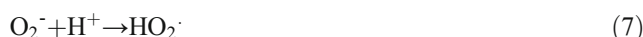


The electrons in the CB of CdSe migrate across the interfacial boundary to the CB of TiO₂. Likewise, the holes generated in the valence band of TiO₂ migrate to the VB of CdSe. The migration of generated opposite charge facilitates charge carrier separation (III) and thus reduces recombination rate [23, 24].



This ensures higher propensity of surface charge with significantly long lifetimes to participate in redox reaction. This imparts enhanced photocatalytic activity to the blend compared to their individual contributions. The transferred electrons in the active sites of TiO₂ react with adsorbed O₂ to form super-oxides (O₂⁻). This superoxide reacts with hydrogen ion to form H₂O₂ and decomposes to generate hydroxyl radicals

(OH[•]) [25]. These radicals have strong oxidation potential to degrade the dye. The reactions are given by



The positively charged hole (h⁺) reacts with OH⁻ or H₂O adsorbed to the surface of TiO₂ to generate hydroxyl radicals [26].



The bulk hydroxyl radicals generated through the superoxide route and the trapped holes route react with any MB transformation products (TP) and the remaining bulk MB to produce simpler molecules (VIII).

Conclusion

Herein, we report the demonstration of photocatalytic reduction of MB dye using a physical mixture of nanoparticles and nanocrystals (TiO₂-CdSe) in the (w/w) ratio: 50:1–9. It was found that at the highest content of the nanocrystals (9 mg), 67% of reduction in the dye concentration could be achieved in a period of 60 min. It is concluded that the presence of CdSe nanocrystals at a mass concentration less than 5% can be used

for remediation of water polluted with industrial dyes. The most interesting conclusion is that physical blend of nanomaterials can exhibit catalytic property superior to their individual contributions.

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