



Enhanced visible light-driven photocatalytic performance of CdSe nanorods

G. Ramalingam^{a,*}, C. Maria Magdalane^b, B. Arjun Kumar^a, R. Yuvakkumar^c, G. Ravi^c,
A. Irudaya Jothi^d, Naresh Kumar Rotte^b, G. Murugadoss^e, Antony Ananth

^a Quantum Materials Research Lab (QMRL), Department of Nanoscience and Technology, Alagappa University, Karaikudi, 630003, Tamil Nadu, India

^b Department of Chemistry, St. Xavier's College, Thirunelveli, 627002, Tamil Nadu-India

^c Department of Physics, Alagappa University, Karaikudi, 630003, Tamil Nadu, India

^d Department of Chemistry, St. Joseph's College (Affiliated to Bharathidasan University), Tiruchirappalli, 620002, Tamil Nadu, India

^e Centre for Nanoscience and Nanotechnology, Sathyabama Institute of Science and Technology, Chennai, 600119, Tamil Nadu, India

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ABSTRACT

Cadmium selenide (CdSe) semiconductor nanorods are prepared in hydrothermal process using hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) and ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$) as reducing agents. The reaction time is increased to 7 h and the amount of hydrazine hydrate used is also increased to 15 mL which have resulted in diminished stacking faults in the CdSe nanorods prepared. The crystal structure, morphological variations, and size of the prepared CdSe nanorods are examined by XRD analysis. The crystalline size of the CdSe nanorods is 20–30 nm in diameter. HRTEM images reveal the formation of high order CdSe nanorods of the length about 25–40 nm. The bandgap in the CdSe nanoparticles is determined to be 2.17 eV. The peak at 595 nm in photoluminescence (PL) spectrum indicates oxygen vacancy defects in the prepared CdSe sample. The variation of dielectric properties with respect to temperature and frequency of pelletized CdSe is studied. High photocatalytic efficiency (98%) of catalyst/ H_2O_2 is also achieved for decomposition of Rhodamine-B dye.

1. Introduction

Cadmium selenide (CdSe) is a binary and primarily, an ionic compound with covalent nature (Cerqueira et al., 1988). The narrow bandgap of the CdSe nanoparticles have attracted greater attention in the recent times which has led to their applications in fields of biomedicine (Vibin et al., 2011), laser (Agarwal and Lieber, 2006), and solar cells (Arjun-kumar et al., 2020). Preparation of chalcogenides have also become prominent in optoelectronic devices. Among the chalcogenides ZnSe, CdTe, and CdSe are prevalent for their photocatalytic activities (Manna et al., 2002). Extensive studies have been reported on CdSe nanorods because of their wider applications in nano-transistors, electrochromic materials, and charge coupling devices (Kazes et al., 2002; Shim et al., 2009; Woggon, 2007). However, to achieve enhanced performance of the rod-like CdSe nanoparticles, it is necessary to adapt novel methods for controlled growth of CdSe rods with prominent structural dimensions (Fitzpatrick et al., 1989; Hyugaji and Miura, 1985) reported heterostructure CdSe nanorods prepared in solution-liquid-solid (SLS) method with 30 nm diameter (Srivatsan, 2012; Manna et al., 2000). Xi et al., (2008) reported that AOT controls the length of the nanorods

whereas reducing agents control diameter of the nanostructures. Murray et al., (1993) achieved CdSe quantum dots/rods using $\text{Cd}(\text{CH}_3)_2$. Therefore it is observed that the $\text{Cd}(\text{CH}_3)_2$ required to be replaced by CdO (Efros et al., 1996). From the environmental viewpoint, solvothermal method is a versatile approach for the preparation of chalcogenide nanorods (Li et al., 1998; Peng and Peng, 2001).

Safer treatment and disposal of pollutants from various industries such as dyes, pesticides, and fertilizers has been an intriguing challenge. Treatment of organic pollutants like dyes from industrial effluents can be done using simple and economically viable processes such as biodegradation, oxidation, absorption, and catalytic wet-oxidation. Photocatalytic degradation has explicitly been a feasible method for the treatment of organic contaminants. Liu et al., (2013) and Wen et al., (2017) reported the degradation of cefalexin with CdSe as photocatalyst. Herein, we report the use of hydrothermal method for the preparation of CdSe nanoparticles which has gained much attention for its exciting advantages in controlling the size, shape, and crystallinity of the nanostructured materials. Increased quantity of hydrazine hydrate is used in the synthesis to optimize the surface morphology and stability of CdSe nanorods (Tang et al., 2002).

* Corresponding author.

E-mail address: ramanloyola@gmail.com (G. Ramalingam).

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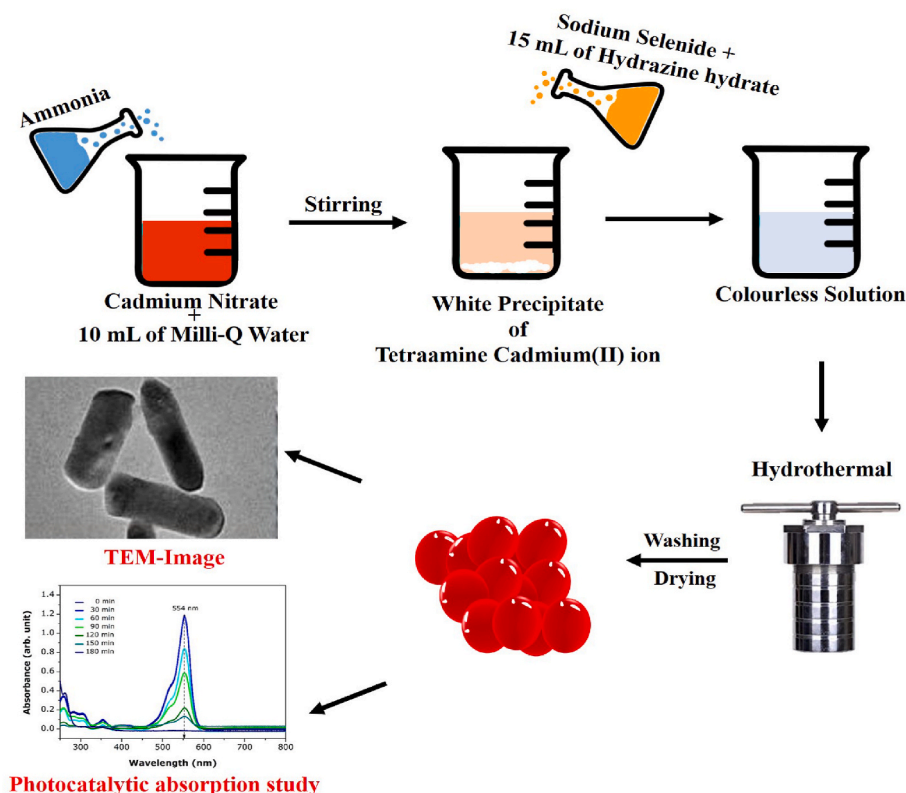


Fig. 1. Schematic diagram of the preparation of CdSe nanorods.

The present work reports the effect of reaction time, increased amount of reducing and complexing agents, and calcination temperature on the synthesis of CdSe nanomaterial and its structural morphology. The application CdSe nanorods as photocatalyst in the decomposition of Rhodamine-B dye is also investigated in the presence and absence of the oxidant H_2O_2 . This article also explores the characteristic changes in the dielectric properties of the CdSe nanomaterials at different temperatures and frequencies.

2. Experimental

2.1. Chemicals and reagents

Cadmium nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, sodium selenite Na_2SeO_3 , hydrazine hydrate $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, and ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) of analytic grade were purchased from Merck. Deionized water is used for preparation of all aqueous solutions.

2.2. Synthesis of CdSe nanorods

Sufficient amount ammonia was added to cadmium nitrate (0.01 M) suspended in 10 mL deionized water to result in the formation of white precipitate, $\text{Cd}(\text{NH}_3)_4^{2+}$ complex. Sodium selenite (0.005 M) stirred for 5 min with 15 mL hydrazine hydrate was then added to $\text{Cd}(\text{NH}_3)_4^{2+}$ complex and mixed well. The pH of the mixture was adjusted in to 11 by adding 0.1 M NaOH solution. It was then transferred into an autoclave, sealed, and kept at 180°C for 7 h. A dark red (maroon) residue formed was calcinated at 400°C for 3 h. The schematic diagram of the synthesis illustrated in Fig. 1.

2.3. Characterization techniques

The X-ray diffraction (XRD) patterns of the CdSe nanorods were measured on Philips X'pert PRO X-ray diffractometer (PW3040/60)

with $\text{CuK}\alpha$ radiation (45 Kv, 40 mA) in the region of $2\theta = 10\text{--}80^\circ$. The surface morphology of the prepared CdSe material was characterized by TEM (model Philips CM12). Absorption and emission spectra were recorded on Shimadzu UV-2550 and PerkinElmer LS-45, respectively. Pellets of CdSe were used for the studies of dielectric properties at different temperature on HIOKI 3532-51 LCR HITESTER in the frequency range 100 Hz - 1 MHz. The dielectric properties were calculated using the formula: $C = k\epsilon_0 A/D$, where C- capacitance; k-dielectric constant; ϵ_0 -permittivity of free space; and D-separation distance. The dielectric constant and the relation between capacitance and dielectric thickness is verified from this measurement.

2.4. Study of photocatalytic efficiency of CdSe nanorods as catalyst

The catalytic efficiency of the prepared CdSe nanorods in photodecomposition of Rhodamine-B under visible light ($>400\text{ nm}$) is studied on a UV-Vis spectrophotometer. 100 mL of Rhodamine-B (10 mg/L) solution is blended with 50 mg CdSe. The pH of the mixture was adjusted to 7.0 and H_2O_2 also was added to produce the hydroxyl ($\text{OH}^\cdot$) radicals and the mixture was irradiated with visible light using a photoreactor lamp. The absorbance of the sample at every 30 min were recorded on the UV-Vis spectrophotometer. The decomposition efficiencies under different conditions were estimated from the plot of C/C_0 vs time of irradiation of visible light (Barber et al., 2009; Das et al., 2018; Rayssi et al., 2018). A calibration curve was plotted to determine the RhB concentration. The colour change from pink to colourless and decreased absorbance provided the evidence for complete degradation of RhB dye (Maria Magdalane et al., 2018, 2017A, 2017B). The RhB dye photodecomposition was observed by using CdSe as catalyst under visible light source (400–800 nm). A visible light (A 300 W halogen lamp) was used as light source (Padmanaban et al., 2021).

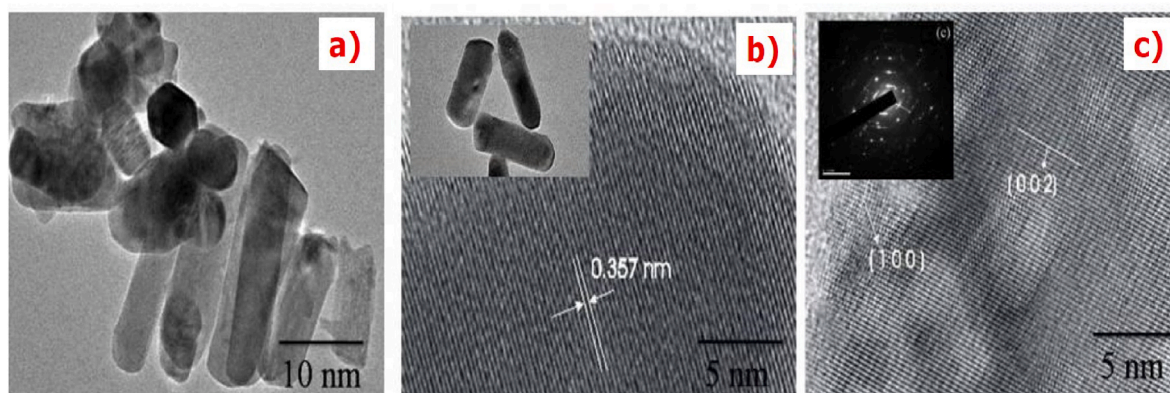


Fig. 2. TEM images of prepared CdSe nanorods with 15 mL hydrazine hydrate and reaction time 7 h.

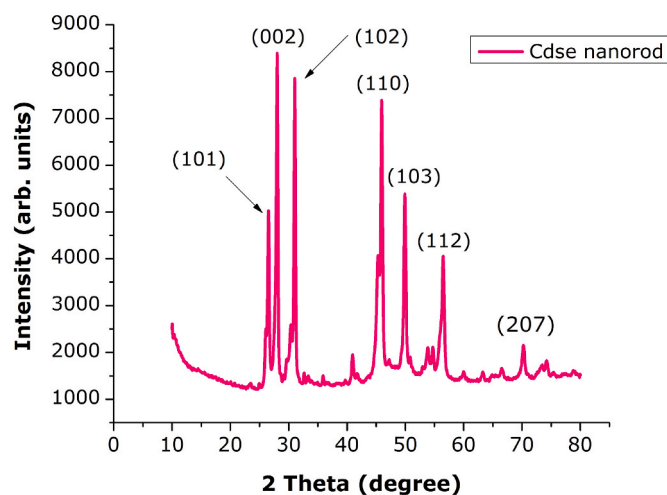


Fig. 3. X-ray diffraction pattern of as prepared CdSe nanorods.

3. Results and discussion

3.1. HRTEM

The surface morphology of the prepared CdSe nanorods was primarily examined by HRTEM (Fig. 2). The synthesized samples exhibit a rod-like structure. The aggregations are similar in the sample with uniform length of about 20–30 nm. HRTEM images reveal the consistency in grain size and shape of the synthesized CdSe at low magnification. The effect of concentration of hydrazine hydrate (HH) on the morphology of synthesized CdSe nanorods is well documented by Manna et al. (2000) and Peng et al. (2000) using the same hydrothermal method at the concentration of HH (10 mL) with the reaction time of 2 h and 4 h. They also reported the presence of significant number of stacking defects in the synthesized CdSe nanorods. However, in the present work we used an increased quantity of hydrazine hydrate (15 mL) and also with an increased reaction time of 7 h and obtained good crystalline and stacking free CdSe nanorods. The synthesized CdSe nanorods have been observed with mean diameter of 7 nm and length of 20–30 nm as depicted in Fig. 2a and b. CdSe nanorods have been formed with regular shape, with reduced number of stacking defects (Fig. 2b) and with lattice fringes at (002) and (100) planes in wurtzite (hexagonal) geometry as visible in Fig. 2c. The selected area electron diffraction (SAED) pattern of CdSe reveals an interplanar distance of 0.3578 nm in the inset of Fig. 2c.

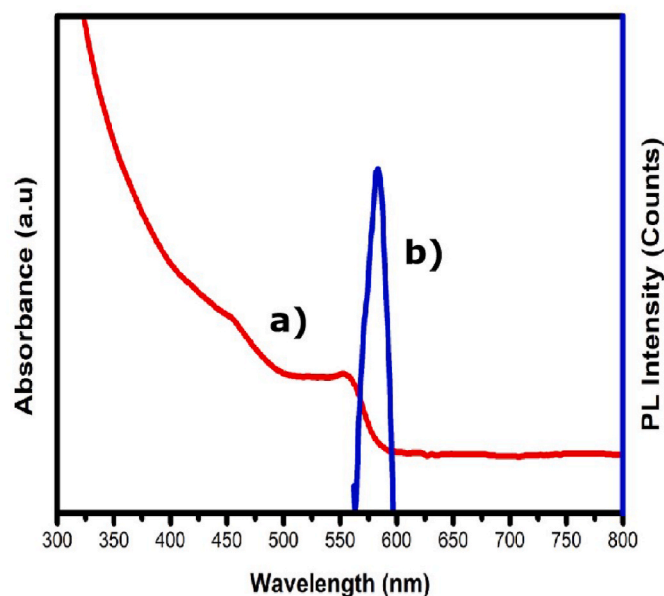


Fig. 4. (a) UV-Visible and (b) photoluminescence spectra of CdSe nanorods.

3.2. X-ray diffraction analysis

The XRD technique is inevitable to investigate the crystallinity of the prepared CdSe nanorods. The wurtzite CdSe nanorods were indexed belonging to (101), (002), (102), (110), (103), (112), and (207) planes (JCPDS Card No.77-2307) (Fig. 3). Highly intense and sharp diffraction peaks observed in the XRD analysis confirm the high crystallinity of the prepared CdSe nanorods. Debye-Scherrer formula $D = 0.9\lambda/\beta\cos\theta$ was employed to calculate the approximate crystallite size (D) of CdSe nanorods which is found to be 20 nm by average. Absence of any other high intensified additional peaks in the XRD patterns reveal the purity of the whole sample and homogeneity of the crystallites (Melnik et al., 2011; Raevskaya et al., 2010).

3.3. Optical properties

The optical properties are significant in screening materials for photocatalytic applications. The smaller bandgap of the CdSe nanorods is an important criterion for its enhanced photocatalytic activity with probable electron-hole recombination. The UV-visible spectra of prepared CdSe nanorods (Fig. 4a) is explored to estimate the band gap $\Delta E_g = h^2/8a^2\mu$, where μ is the reduced mass of CdSe ($m_e = 0.13m_0$; $m_h = 0.3m_0$), a is the diameter for CdSe nanorod (25 nm) and h is Planck's

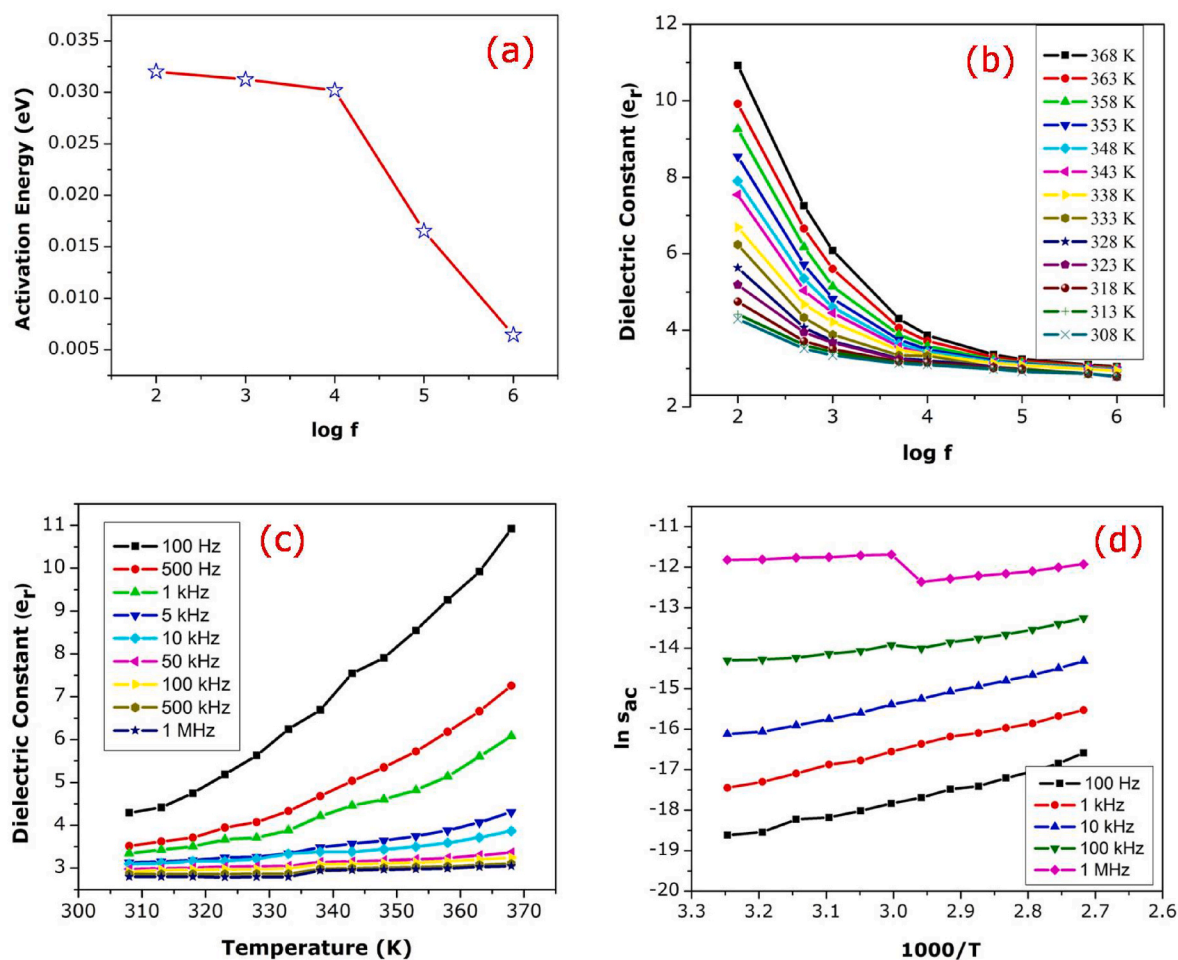


Fig. 5. (a) Frequency vs activation energy, (b) frequency vs dielectric constant, (c) dielectric constant vs temperature, and (d) electrical conductivity vs temperature. The parameters for the CdSe nanorods are measured on Hioki 3532-50 LCR Histester instrument.

constant. The absorption band at 570 nm is shifted slightly towards lower wavelength indicating a change in the bandgap energy. Photon absorption with greater or equal to the bandgap of cadmium selenide leads to more photoexcited electrons and reveals the ability of the synthesized CdSe rods towards its application as photocatalyst in the degradation of organic molecules (Liu et al., 2013). Further, it also observed a very small hump around 450 nm in the UV–visible spectrum which is due to first (1s–1s) exciton transition during valence and conduction band (Fendler, 1987) as a consequence of the quantum size effect and threshold wave length of band function of nanoparticle size (Wang and Herron, 1991; Pedone et al., 2005). The intensified absorption of visible light by CdSe nanorod is observed with a bandgap of 2.17 eV which may lead to better photocatalytic performance due to the probably higher charge transfer from bulk to nanoparticle surface. The broadening in the bandgap of the catalyst is due to the quantum size effect. Smaller size of the CdSe nanorods ascribes to its evolution or aggregation since the crystal size is a key factor for photocatalytic process (Wang et al., 2014).

3.4. Photoluminescence studies

The photoluminescence spectrum of the prepared CdSe nanorods shows an intense peak at 595 nm (Fig. 4b) which is blue shifted in comparison with 716 nm for wurtzite structure sample (Inamdar et al., 2008; Kucur et al., 2003) indicating the presence of oxygen vacancy defects in the prepared CdSe sample (Tongay et al., 2013). The results of the photoluminescence study is also supported by the HRTEM images

which revealed a reduced number of non-stacking faults in synthesized nanorods (Amelia et al., 2011). Since, the nanorod structure of the prepared CdSe is characterized with larger active surface area, it exhibits enhanced photocatalytic performance. Therefore, photoluminescence spectra displayed that the peaks at higher wavelength attributed to crystalline structure defects like oxygen vacancies.

3.5. Dielectric measurements

The dependence of dielectric constant of CdSe nanorod samples on the frequency and temperature is illustrated in Fig. 5a–d. Because of the bonding and local lattice diffusion between constituents, the CdSe sample show higher activation energy (Fig. 5a). Hence, volume diffusion through the frequency phase is easier than lattice diffusion through solid phase. The domination of volume diffusion through the frequency phase has a significant effect in drastically lowering the activation energy of CdSe nanocrystals while increasing the frequency. Fig. 5d depicts a linear relation between $\ln \sigma_{ac}$ and $1000/T$. The activation energies are achieved in the range of 0.005–0.038 eV over 100 Hz to 1 MHz.

The frequency dependence of dielectric constant of CdSe nanoparticles with varying temperature is given in Fig. 5b. Low dielectric constant at higher frequencies is suitable for applications in solar cells, photonic and electro-optic devices, and photocatalysis (Kamat, 2007; Peng et al., 2000). The temperature dependence of dielectric constant of CdSe nanoparticles with varying frequencies is given in Fig. 5c. The dipoles altered by the applied electric field results in larger dielectric constants at low frequencies and at high temperatures (Chawla et al.,

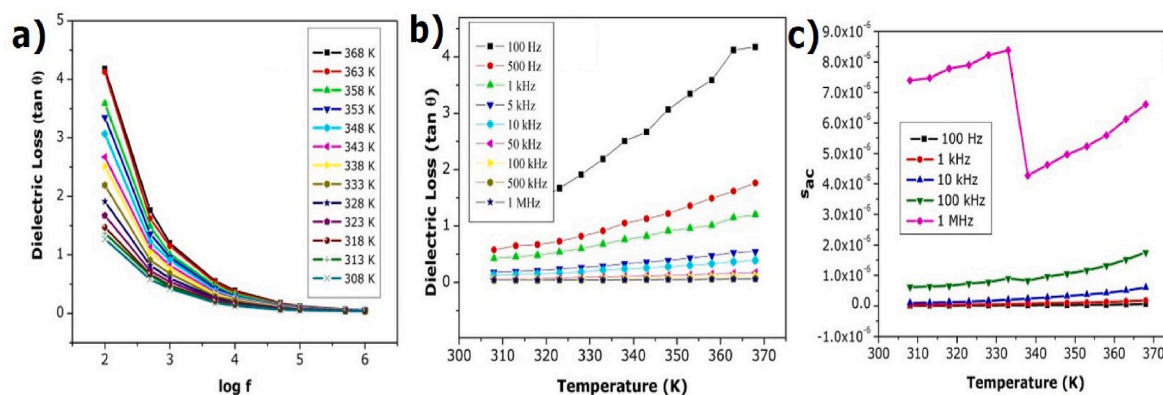


Fig. 6. Plots of (a) dielectric loss vs frequencies at different temperatures, (b) dielectric loss vs temperature at different frequencies, and (c) electrical conductivity vs temperature at different frequencies. The parameters for the CdSe nanorods are measured on Hioki 3532-50 LCR Hiester instrument.

2007). The dielectric loss variation against frequency at different temperatures is presented in Fig. 6a–c. The dielectric loss decreases rapidly at lower frequencies and is constant at higher frequencies. In terms of temperature dependence, dielectric loss is increased because of increased mobility of charge carriers caused by rise in polarization (Rayssi et al., 2018). At higher frequencies, the observed low dielectric loss is enabled by the purity of the CdSe with minor defects. Electrical conductivity is a dynamic feature that discloses information about the transport phenomenon in semiconductors. A raise in electrical conductivity of CdSe at low-frequency studied by varying temperatures is illustrated in Fig. 6c (Das et al., 2018). Nevertheless, at high frequency, particularly in 1 MHz region, a sudden increase in conductivity is noted which must be related to polaron hopping of charge carriers bound in localized states (Barber et al., 2009).

The photocatalytic mechanism explains the relationship between the photocatalytic and the dielectric constant as follows: The larger dielectric constant of the photocatalyst having longer the photoelectron lifetime. As a result, through stimulated emission and spontaneous emission, the transition of photoelectrons from the conduction band to the valence band to combine with the holes becomes more difficult, facilitating effective production of hydroxyl free radicals via sufficient oxidation of hydroxyl ion and water by the holes on the photocatalyst surface (Ahmad et al., 2017; Farooq et al., 2019).

3.6. Photocatalytic degradation of Rhodamine-B dye using CdSe nanorods

Several methods have been practised for decomposing carcinogenic-related dyes and pigments. The accumulation of such pollutants become a significant primary source for all types of pollution in the environment these days. Laatar et al., (2017) used CdSe nanorod/TiO₂ to enhance solar- and visible-light photocatalytic activity. Liu et al., (2013) has explored the CdSe quantum dots for the degradation of Cefalexin. The observed degradation was found to be 70 %. Wen et al., (2017) investigated the photo-induced carriers separation efficiency and mechanism in vesicle CdSe nano-semiconductor photocatalysts. Nevertheless, in the present degradation process, highly carcinogenic Rhodamine-B dye was decomposed in CdSe nanorods as a catalyst in visible light irradiation (Magdalane et al., 2016).

In the present work, 100 mL Rhodamine-B (10 mg/L) was blended with 50 mg catalyst at pH~7. The sample was placed in the photoreactor for visible light irradiation. The absorbance of the sample at every 30 min were recorded on the UV–Vis spectrophotometer. The decomposition efficiencies under different conditions were estimated from the plot of C/C₀ vs time of irradiation of visible light. The colour change from pink to colourless and decreased absorbance provided the evidence for complete degradation of RhB dye (Maria Magdalane et al., 2018, 2017A,

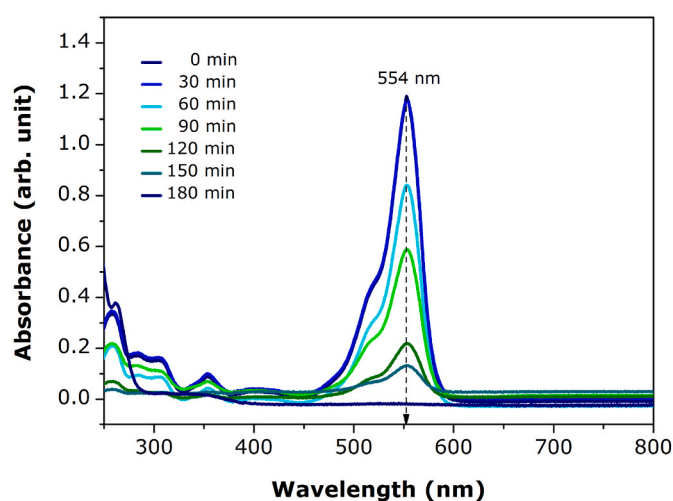


Fig. 7. UV–Vis absorption spectra for RhB dye recorded at the time interval of 30 min to monitor the photocatalytic degradation of RhB dye using the prepared CdSe nanorods.

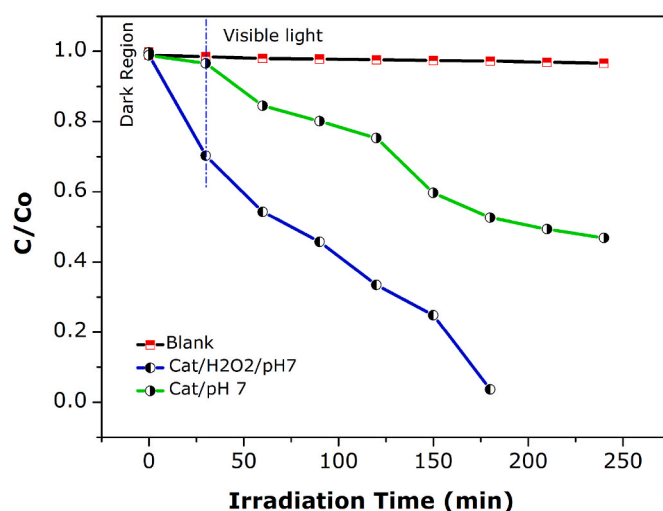


Fig. 8. Irradiation time versus degradation of RhB dye using CdSe nanorods at pH 7 with H₂O₂ and without H₂O₂.

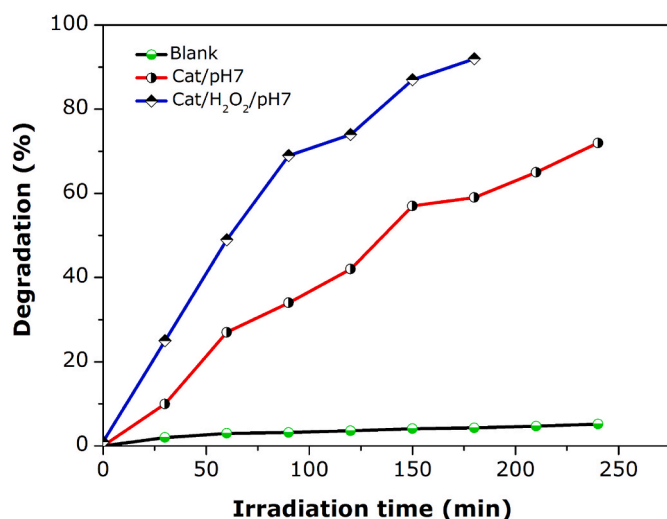


Fig. 9. Plots of degradation vs irradiation time for the photocatalytic degradation of RhB dye using CdSe nanorods at pH = 7 with H₂O₂ and without H₂O₂.

Table 1

Efficiency of various CdSe materials in the photocatalytic degradation of RhB.

Nanomaterial	Deg. Time (min)	Deg. (%)	Light source	Cat (mg)/ (mg/L) Dye, mL Dye<	Ref.
CdSe@electrospun carbon nanofibers	90	81	Xenon lamp (200 W)	50/10, 50	Panthi et al., (2020)
CdSe-graphene composite	150	56	LED Light	0.5/5, 150	Ghosh et al., (2013)
ZnO/CdSe nanocomposites	180	99	Xenon lamp (100 W)	1.5/10, 100	Abbas Alshamsi et al., 2021
CdSe nanorod/TiO ₂	150	98	Simulated solar light irradiation (5 mW/cm ²)	50/10, 50	Laatar et al., (2017)
CdSe-Microspheres	300	72	Visible light	50/10, 50	Gong et al., (2019)
CdSe Nanorods	240	78	Visible light	50/10, 100	Present Work
	180	98	Visible light with H ₂ O ₂	50/10, 100	

2017B). Similar experiment was carried out with 5 mL H₂O₂, and the efficiency is recorded. The photocatalytic degradation efficiency (η) plotted against time at neutral pH (7.0) is given in.

Figs. 7–9. The degradation efficiency of RhB dye is 78% when only CdSe is used as the catalyst and the time taken for complete decolorization is 240 min, while degradation efficiency is 98% and the time taken for decolorization is 180 min for the catalyst/H₂O₂ combination (Fig. 9). A comparative photocatalytic efficiency of the CdSe materials used for degradation of Rhodamine-B is presented in Table 1. Interestingly, the pure CdSe nanorod form presented in this work exhibits higher degradation efficiency.

3.7. Mechanism of photocatalytic decomposition of RhB with CdSe nanorods

The mechanism involved in the visible light photon-induced catalysis of the decomposition of RhB is illustrated in Fig. 10. Hemmateenejad et al., (2015) has synthesized starch-capped CdSe with exceptional performance and Wen et al., (2017) has explained the vesicular CdSe nano-semiconductor and its possible photocatalytic microprocess mechanism. However, the CdSe nanorods catalyst consumes highest energy photons to generate excitons. The charge transportation on CdSe nanorods helps degradation of dye molecules driven by visible-light. Valance band (VB) and conduction band (CB) of CdSe nanorods are calculated using equations (1) and (2).

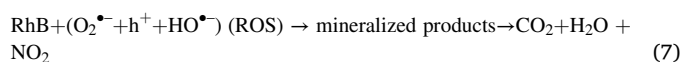
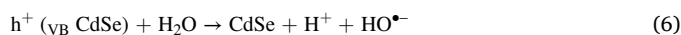
$$E_{CB} = \chi - E^C - 0.5E_g \quad (1)$$

$$E_{VB} = E_{CB} + E_g \quad (2)$$

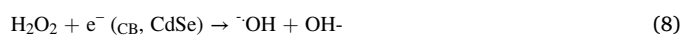
where χ - absolute semiconductor electronegativity, E^C - free electrons energy on NHE (Normal Hydrogen Electrode ~4.5 eV). E_g - CdSe nanorods energy bandgap. And χ is calculated from the equation:

$$\chi = [(A)_a(B)_b(C)_c]^{1/(a+b+c)} \quad (3)$$

where a, b, and c - number of atoms in compounds. Thus, calculated VB and CB edge potentials of the CdSe nanorods are 1.73 and -0.445 eV, respectively. The electrons in the valence band are rapidly photo-generated by capturing energized photons during irradiation of visible light and are transported to the conduction band. Panthi et al., (2020), Sun et al., (2020) has explored the mechanism on the exposure of visible light and Wang et al., (2014) reported the mechanism with CdSe QDs. Thus, the synthesized cadmium selenide results in the generation of electron-hole pairs on CdSe nanorods surface. The electrons (e^-_{CB} CdSe) effectively lead to photo-reduction while the holes (h^+_{VB} CdSe) facilitate the photo-oxidation in the decomposition of RhB dye (Wen et al., 2017). Further, electrons on conduction band take up surface oxygen to generate superoxide radicals. Subsequently, the CdSe is greatly excited by visible light and results in greater photocatalytic effect on the decomposition of organic dye. Initially, the dye molecules are adsorbed over the catalyst surface and the holes in the valence band initiate oxidation of RhB dye (Maria Magdalane et al., 2018, 2017A). The generated hydroxyl radicals (OH) and superoxide radicals are highly accountable for decomposing organic dyes by yielding water, carbon dioxide, etc. as shown in the following equations (4)–(7).



Besides, the nanorod catalyst assists in generating a different reactive oxygen species by the addition of H₂O₂ and speeds up electron utilization and creates more holes for the oxidation of RhB dye molecules.



The amount of oxidant is a key factor for the degradation of RhB dye solution and influences the catalytic performance of dye degradation. Therefore, the photocatalytic reaction needs the oxidant hydrogen peroxide that may react with a higher amount of dye solution. The results from the photocatalytic studies also reveal the enhanced catalytic performance of the synthesized CdSe nanorods and the significant influence of the hydrogen peroxide in the degradation of RhB dye

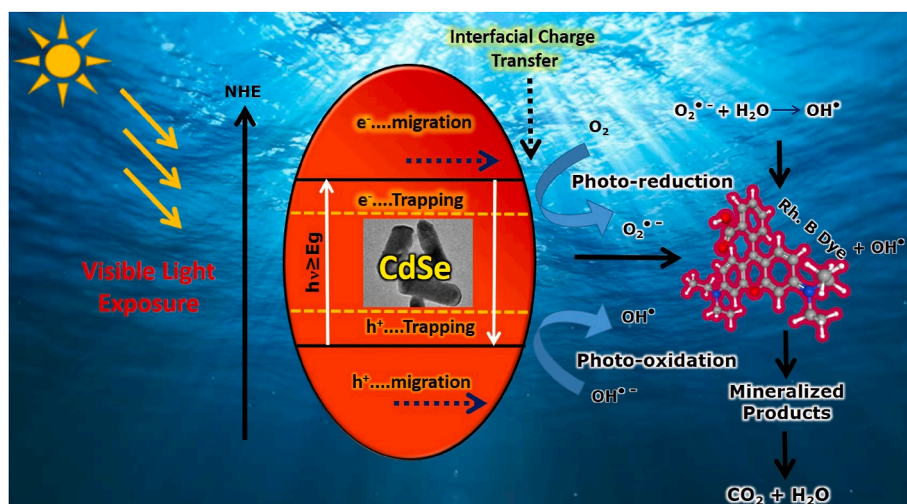


Fig. 10. Plausible mechanism of photodegradation of RhB using CdSe nanorods as catalyst using H_2O_2 .

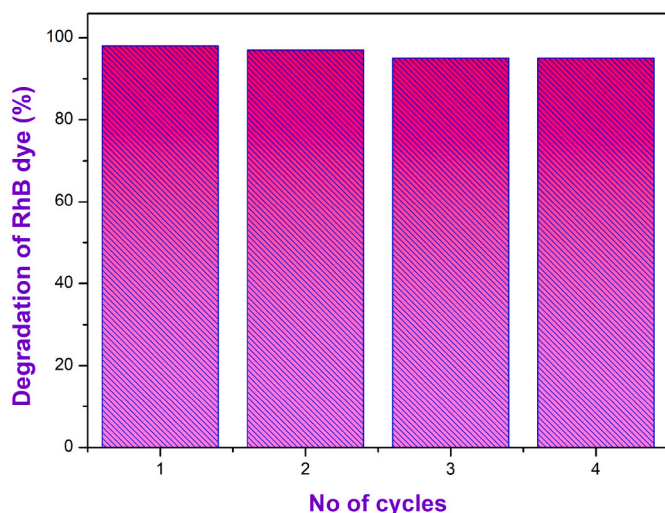


Fig. 11. Reusability of CdSe nanorods as photocatalyst on the degradation of RhB dye.

(Ramalingam et al., 2020).



3.8. Reusability studies

In photocatalytic studies, the reusability of produced CdSe nanorods plays a most important role since it is proficient to contribute for the degradation of the dye and diminish the cost of the entire waste water treatment. To inspect the stability of the catalyst, four consecutive cycles of the degradation of RhB dye were carried out using the same used CdSe nanorods catalyst. In each new cycle fresh RhB dye was used. The catalyst was removed from the experimental solution by filtrations. The observed result from all the four-cycle experiments of the CdSe nanorods was depicted in Fig. 11. The overall outcomes showed that there is no heavy loss of catalytic amount, which remains constant even at the end of the fourth cycle with almost the same photodecomposition dye

solution, which proves the high stability of CdSe nanorods.

4. Conclusions

Highly ordered CdSe nanorods prepared by hydrothermal process. CdSe nanorods exhibit blue shift compared to bulk materials which is confirmed from both the UV-Vis and PL spectra. The energy band gap is 2.17 eV from the calculated absorption spectrum. The percentage of dye degradation increases with irradiation time, which indicates that the synthesized sample can be a promising photocatalyst for pollution mitigation. Higher catalytic efficiency (98 %) of the CdSe nanorods is demonstrated with H_2O_2 at pH 7.0 in the photodecomposition of RhB dye than the catalyst without H_2O_2 (78%). Also, the synthesized CdSe sample exhibits higher stability on its reuse in the photodegradation of organic dye.

Credit author statement

G. Ramalingam: Supervision, C. Maria Magdalane: Methodology, B. Arjun Kumar: Writing – original draft, R. Yuvakkumar: Supervision, G. Ravi: Conceptualization, A. Irudaya Jothi: Investigation, Naresh Kumar Rotte: Validation, Antony Ananth: Methodology, G. Murugadoss: Conceptualization.

Declaration of competing interest

All authors hereby declare that there is no conflicts of interest.

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