Chapter 3

Photocatalytic oxygen evolution reaction for energy conversion and storage of functional nanomaterials

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3.1 Introduction

Rare earth metal oxides have been used extensively in various applications such as environmental, energy, and biomedical services due to their specific properties such as grain size, elemental configuration, and self-organized structures \cite{1-3}. Current research focuses on cerium oxide nanostructure, due to the low energy bandgap between Ce\textsuperscript{3+} and Ce\textsuperscript{4+} states in cerium oxide along with their high oxygen mobility and high oxygen storage
capacity [4]. These properties make them suitable for applications in various fields, as gas sensors, optoelectronics, catalysts, fuel cells, and solid-state electrolytes [5]. There is numerous technically projected synthesis of nanosized ceria such as heterogeneous catalysts by chemical redox reaction, thermal approach, sonochemical method, hydrothermal method, sol-gel process, and self-assembled nanoprocesses [6]. Among these, the hydrothermal method is widely used, because of the formation of homogenous nanopowder as the initial product with a fine grain size [7,8]. In general, the photocatalytic efficiency increases by incorporating the heterostructures [9]. Because, heterocomposites prepared can fine tune the electronic properties of the photocatalyst by separating the electron-hole pairs in an efficient manner.

CeO$_2$ with transitional metal oxide (TMO) have gained much attention because of their attractive optical possessions and photogenerated charge carriers, which may be enhanced in the CeO$_2$ matrix [10–12]. The exceptional nanostructure morphology and mesoporous nature of cerium with 3d transitional metal ions (TMO) allowed them to become a solar material [13]. When the transition metal ion in lower valance state than 4$^+$ is collectively dispersed into the ceria matrix, the arrangement of atoms becomes dense and this changes the electronic conductivity of metal ions [14,15]. However, to enhance various properties of CeO$_2$ nanomaterials, it is desirable to condense the atom size and enhance the growth of the energetic superficial zone [16]. A decrease in particle size augments the electrical conductivity and sensing and catalytic properties of nanomaterials [17]. Here a simple chemical precipitation assisted hydrothermal method without any surfactant has been a cause of stimulation of cerium, cadmium multifaceted nanomaterials with higher surface area and the effective claims [18,19]. This simple method is alternative to the chemical methods with surfactant which are very costly as well as emit hazardous byproducts which can have adverse effect on the environment [20]. Therefore we tried to fabricate CeO$_2$/CdO nanomaterials with high active surface area and less particle size using cost effective hydrothermal method [21,22]. In polluted waste waters elimination of organic dye contaminants is necessary, because of the nonbiodegradable nature of the pollutants [23]. Toxic organic dye degradation using semiconducting materials in the existence of UV/visible light studied worldwide [24]. Convention of herbicides, pesticides, and various synthetic dyes are widely polluting the environment [25–28].

The organic pollutant like Rhodamine-B (RhB) dye has been used in productions and in our day-to-day life and the RhB dye produces carcinogens like aminobenzene [29]. The contamination of the physical and biological components of the earth/atmosphere system to such an extent that normal environmental processes are adversely affected [30]. Hence highly carcinogenic organic compounds and their detoxification are critical to the situation and this development converts existing research to preserve human health and security [31]. Thus an efficient method to discard these organic contaminants from the
various waste materials is needed [32]. The photocatalytic degradation (PCD) of toxic organic dyes using catalyst such as TiO$_2$, ZnO, CuO, CeO$_2$, etc., in UV/visible and xenon beams source is considered a highly effective method [33,34]. Among the various photocatalysts, cerium oxide-containing transition metal oxides have proven to be very efficient. Rare earth/transition metal oxide is easier to recover from aqueous systems due to its higher molecular weight [35]. To understand the formation of heterostructured CeO$_2$/CdO binary metal oxide nanostructure, it is necessary to examine the influences of the preparation conditions [36]. Since this is not dealt with much in the literature, here we analyze the influence of preparation parameters on the synthesis of heterostructured CeO$_2$/CdO binary metal oxide nanostructures [37,38]. The exact mechanism of the degradation of dyes by nanostructures is important to understand, but the pathway of decomposition of synthetic dye during the whole process is still not clear and more investigations are needed to characterize the various properties of CeO$_2$/CdO multilayered nanomaterials [39]. Hence, in this present work, we prepared a binary metal oxide CeO$_2$/CdO nanostructure with almost uniform size of clusters by hydrothermal technique in different ratios, which were studied for the decomposition of water source and organic dye in aqueous system illuminated with UV/visible light [40]. Also, the synthesized nanomaterial with small grain size and large active surface area was examined against A549 (human lung epithelial cell).

### 3.1.1 Structural investigation of CeO$_2$/CdO nanostructures

The X-ray diffraction (XRD) of the chemical precipitation followed hydrothermal technique synthesized CeO$_2$, CdO, and CeO$_2$/MO binary metal oxide in 1:1, 2:1, and 1:2 molar ratios correspondingly is shown in Fig. 3.1A. All the peaks can be assigned to either CeO$_2$ or CdO phase and there are no other new phases. This high-purity binary metal oxides reveal that the major peaks of CeO$_2$ has $2\theta = 28.70, 33.08, 47.51, 56.44, 59.08, 69.47, 76.70,$ and $79.07$ degrees corresponding to the (111), (200), (220), (311), (222), (400), (331), and (420) planes and has cubic fluorite structure in which each metal cation is surrounded by eight oxygen atoms (space group Fm-3m JCPDS Card No. 34-0394). CeO$_2$ shows a dominant and high intense peak on (111) plane, which needs high energy to form oxygen vacancies on (111) planes than the less intense peak and they are highly stable. There was no evidence of the presence of Ce$_2$O$_3$ phase. The diffraction peaks at $2\theta$ values of $33.08, 38.43, 55.31$, and $65.90$, and $69.28$ degrees correspond to pure CdO matching the (111), (200), (220), (311), and (222) planes with cubic structure (JCPDS Card No. 05-0640), thus indicating the formation of CeO$_2$/CdO nanostructure with excellent crystalline nature. The strength and locations of the peaks are in perfect arrangement with the literature values. The decrease in the
The intensity of CdO peaks indicates that CeO$_2$ is formed on CdO surface and the increase in the ceria peak intensity suggests the larger crystallite sizes. The XRD pattern of the sample shows no satellite peaks belonging to Ce (OH)$_3$ and hexagonal Ce$_2$O$_3$, thus indicating a complete conversion of the sample into cubic fluorite ceria. The crystallite size of metal oxides was calculated using Debye–Scherer’s formula \( D = \frac{0.9 \lambda}{\beta \cos \theta} \), where \( D \) is the crystallite size, \( \lambda \) the wavelength of X-rays, \( \theta \), the Bragg diffraction angle, and \( \beta \), the full-width at half-maximum (FWHM) of the diffraction peak. The CeO$_2$/CdO nanostructures showed only cubic phase, which confirms the composition of CeO$_2$ and CdO in the heterostructure, and it is in good agreement with early reported work. To establish charge balance, extra positive ions must be introduced into the grain surface. Therefore the CeO$_2$ and CdO are in the form of composites rather than as solid solution.

### 3.1.2 Fourier transform infrared spectroscopy

The Fourier transform infrared spectrum of CeO$_2$ mixed with CdO heterostructured binary nanostructures in different ratios (1:1, 1:2, and 2:1) is shown in Fig. 3.2A in the wavelength range of 3700–400 cm$^{-1}$. The extensive band
in the range of 3600 cm$^{-1}$ is due to the OH stretching of water molecules [41]. The broad peak at 450−700 cm$^{-1}$ is due to the characteristic stretching of Ce−O bond and the frequency is reduced due to the formation of mixed binary metal oxide [42]. The peaks at 800−1500 cm$^{-1}$ are assigned to CdO [23,43]. The band at low-frequency regions below 1400 cm$^{-1}$ corresponds to the formation of doped CeO$_2$/CdO nanomaterial. The absorption peaks between 1500 and 1700 cm$^{-1}$ are attributed to the twisting vibration of the adsorbed H$_2$O molecules [44].

3.1.3 Field emission scanning electron microscopy studies

The comprehensive superficial morphology and effect of size and shape of CeO$_2$ mixed with CdO in different molar ratios (1:1, 1:2, and 2:1) were examined by field emission scanning electron microscopy (FESEM) analysis. All the synthesized samples with different molar ratios form different
Field emission scanning electron micrographs of CeO$_2$/CdO nanostructures at different magnifications for the prepared samples by hydrothermal method are presented in Fig. 3.3A-L. Fig. 3.3G and H shows that the FESEM images of CeO$_2$ are highly porous material with irregular shapes. Fig. 3.3I and J shows the surface morphology of CdO, which has agglomerated crystal phases. The FESEM images in Fig. 3.3A and B of binary metal oxide Ce$_{1}$/Cd$_{1}$ nanostructure have spherical and heterogeneous phase distribution with more cavities. The particle size is in the range of 15–40 nm with good porous morphology. Fig. 3.3C and D shows that the FESEM microstructures of Ce$_{2}$/Cd$_{1}$ binary metal oxide have small spherical shape nanoparticles with aggregated morphology. The particle sizes are in the range of 5–30 nm, respectively. A small variation was identified by FESEM and XRD, since FESEM calculations are based on the difference between the visible grain boundaries, whereas XRD calculations measure the extended crystalline region that diffracts X-rays coherently [43]. The FESEM images of Ce$_{1}$/Cd$_{2}$ binary metal oxide show that the particle is aggregated, which is due to the excess of cadmium metal oxide shown in Fig. 3.3E and F. The minimum changes in the particles size could be due to the particle aggregation [45]. Due to the morphological evolution of CeO$_2$/CdO nanostructures with different conditions. Elemental analysis was done along with FESEM using the EDX technique. EDX analysis revealed the
peaks of the elements in the nanostructure. This data helped to ensure that the cerium oxide and cadmium oxide synthesized by various routes resulted in CeO$_2$/CdO nanostructures. The EDX spectra showed no other elements, thus confirming the purity of the phase in the composite [46]. It is in good agreement with the XRD analysis.

3.1.4 High-resolution transmission electron microscopy studies

The microstructures of the CeO$_2$, CdO, and CeO$_2$/CdO nanomaterials in different ratios (1:1 and 2:1) were analyzed by high-resolution transmission electron microscope (HRTEM). Pure CeO$_2$ and CdO metal oxides have an irregular shape as shown in Fig. 3.4A and F. Fig. 3.4G–J shows the HRTEM images of Ce$_2$/Cd$_1$ nanostructure and Fig. 3.4B–E shows the HRTEM images of Ce$_1$/Cd$_1$ nanostructure prepared by hydrothermal method, and the selected area of electron diffraction pattern is shown in Fig. 3.4E and J. The fine particle is the aggregate of nanocrystallites and the shape is spherical, and it reveals the polycrystalline cubic crystal structure [47,48]. Fig. 3.4C shows that the particles are more agglomerated with irregular shape. Fig. 3.4G and H shows that the nanomaterial is monodispersed with the spherical shape. From the HRTEM image it can be seen that the particle diameter is in the range of 25–5 nm, which is consistent with XRD results [49]. There is a slight difference in the average particle size of the samples, which is due to the agglomeration of nanomaterials. Hence, the prepared CeO$_2$/CdO nanostructures have a particle size in the range of 5–30 nm using the hydrothermal method [50].

3.1.5 Diffuse reflectance spectroscopy studies

The optical possessions of pure CeO$_2$, CdO, and mixed heterostructured CeO$_2$/CdO metal oxide nanostructures with different ratios (1:1, 1:2, and 2:1) have been studied by UV–visible [diffuse reflectance spectroscopy (DRS)] dimensions; the results are shown in Fig. 3.5A and B. To evaluate the bandgap of the synthesized nanostructures, diffuse reflectance spectroscopy was obtained in the wavelength ranges of 200–800 nm [51]. The bandgap energy is determined by appropriately fitting the data to the shortest transition equation, $(\alpha h\nu) = A(h\nu−E_g)^n$, where “$\nu$” is the frequency, “$A$” is a constant, and “$n$” can have values 1/2, 3/2, 2, and 3 depending on the mode of interband transition (i.e., through acceptable and direct forbidden, indirect allowed, and indirect forbidden transitions, respectively). The bandgap of the nanomaterials has been inferred from the altered Kubelka–Munk (K–M) function plots. The reflectance data ($R$) stated as $R(h\nu)$ have been attained by the submission of the K–M algorithm. In UV, visible diffuse reflectance absorption spectra, $(F(R)h\nu)^{1/2}$ versus photon energy design gives indirect bandgap and $(F(R)h\nu)^{2}$ versus photon energy plot signifies a direct bandgap.
FIGURE 3.4 HRTEM images of CeO$_2$/CdO nanostructures: (A) pure CdO, (B–E) Ce$_{1}$/Cd$_{1}$, (F) pure ceria, and (G–J) Ce$_{2}$/Cd$_{1}$. 
FIGURE 3.5 DRS spectra: (A) direct bandgap for pure CeO$_2$, CdO, Ce$_1$/Cd$_1$, Ce$_1$/Cd$_2$, and Ce$_2$/Cd$_1$; (B) indirect bandgap of pure CeO$_2$, CdO, Ce$_1$/Cd$_1$, Ce$_1$/Cd$_2$, and Ce$_2$/Cd$_1$ nanostructures.
transition [52]. Both direct and indirect bandgap vitalities are originating to be abridged with the particle size and morphology of nanomaterials, when associated to the discrete metal oxides. Hydrothermally synthesized CeO$_2$/CdO nanosamples display the bandgap of 3.19, 3.15, 2.98, and 2.89 eV, respectively. The variations in the bandgap energy are due to the different preparation techniques, with average grain values, shape, and structural complaint in the lattice [53]. The optical possession of the absorbance of cerium oxide/cadmium oxide in the UV region proves that it may be used as a respectable entrant for UV absorbing materials [54]. Cadmium oxide with cerium oxide could decrease the bandgap of cerium increasing the growth amount of Ce$^{4+}$ states, subsequent to the formation of contained vigor states that are closer to the conduction band. The peak at 400 nm confirms the fluo-rite cubic structure of nanostructures, revealing the quantum size effect (QSE) of the blue shift modification in the UV-visible spectrum [55]. Hence, there is a transition of electron between the O 2$p$ and Ce 4$f$ states in O$_2^2$ and Ce$^{4+}$.

### 3.1.6 Micro-Raman spectroscopy

To evaluate the molecular motion of nanomaterials, Raman vibrational spectroscopy was used to classify and determine the structural symmetric of the molecules. Raman spectroscopy helps in determining the inelastic scattering of a monochromatic scattered light. CeO$_2$ nanoparticles displayed a solid intense band at 434 cm$^{-1}$, which represents the F$_{2g}$ Raman active mode of fluorite type-like cubic structures [56,57]. The structural characterization of the CeO$_2$/CdO nanostructures is clearly seen in Fig. 3.6A and B, which shows the broad band at 464 and 815 cm$^{-1}$ laterally with a weak absorption peak at 300, 370, 500, 605, 734, 780, and 864 cm$^{-1}$. The band at 464 cm$^{-1}$ mostly resembles the F$_{2g}$ Raman active mode of cubic fluorite structure, which proves that the synthesized nanomatrix clearly has a crystalline fluo-rite cubic structure [58,59]. The peaks of the ceria metal oxides occur at higher wave number with high concentration of other metal oxides. The shift in the peak position is due to residual stress and the presence of other M$^{2+}$ metal matrix. This also shows that the CeO$_2$/CdO nanostructure has advanced oxygen defects [60]. Hence, Raman spectroscopy is a promising tool for the structural elucidation of CeO$_2$/CdO nanostructures can be used to differentiate the different phase modes.

### 3.1.7 Photoluminescence spectra

The photoluminescence (PL) spectra of CeO$_2$ and CeO$_2$/CdO metal oxide nanostructure with different molar ratios 1:1, 1:2, and 2:1 are shown in Fig. 3.7A–D, with an excited wavelength of 290 nm. The captured emission spectra for pure CeO$_2$ are in the range of 250 nm for the short wavelength to
FIGURE 3.6 μ-Raman spectrum of CeO$_2$/CdO nanostructures: (A) pure ceria and (B) Ce$_2$/Y$_1$.
FIGURE 3.7 Photoluminescence (PL) spectrum of CeO$_2$/CdO nanostructures: (A) pure ceria, (B) Ce$_1$/Cd$_1$, (C) Ce$_2$/Cd$_1$, and (D) Ce$_1$/Cd$_2$. 
400 nm for the long wavelength [61]. By the addition of CdO, the emission peaks appeared at 400–450 nm in the red region spectrum with additional changes in the broadness of the peak positions occurring at room temperature. The emission spectra of CeO₂/CdO were characterized by major peaks near 240, 260, 280, 380, 417, and 445 nm. All emission spectra showed a prominent peak at 445 nm that was attributed to oxygen-related defects in the CeO₂/CdO at microscopy level [62]. The intensity of the emission band at 445 nm increased with increasing CdO content in the CeO₂/CdO nanostuctures. The violet band around 402 nm for the CeO₂ nanostructures initiates from the defect states current widely among the Ce 4f state and O 2p valence band [63]. The two blue emissions at 417 and 445 nm are connected to the plentiful flaws such as displacements, which is supportive for fast oxygen transference. At room temperature, electron transition results mostly from imperfections level to O 2p level [64]. The quantum confinement effect was pragmatic by earnings of PL spectroscopy, which stretches the nearby subbandgap defect states and excitation spectra of the pure nanoparticles. The superficial situations and concentration of defects can modify with the developed circumstances, textural morphology, size, and shapes of nanocrystallites [65].

3.1.8 X-ray photoelectron spectroscopy studies

The oxidation state of each element in the sample as well as the composition of the surface functionalization of the Ce₂/Cd₁ nanostructure was examined by X-ray photoelectron spectroscopy (XPS). The obtained XPS results show (Fig. 3.8) that the peaks correspond to C (1s), O (1s), Cd, and Ce (3d) for CeO₂ NPs. The C (1s) signals are mainly expected due to trace quantity of

![XPS spectrum of Ce₂/Cd₁ nanostructure.](image)
surface humidity and absorption of organic contaminants during handling. CeO$_2$ nanosphere has the binding energy bands at 872.66, 887.85, 906.14, 922.14, 930.52, 916.34, and 921.33 eV. These spectra were found to be fully consistent with those reported previously [66]. The lower energy level of O (1s) signal at 529.13 eV is attributed to O$^{2-}$ ions surrounded by Ce$^{4+}$ ions, which corresponds to the Ce–O bond in CeO$_2$. The middle energy level of O (1s) at 533.86 eV can be ascribed to the O$^{2-}$ ions in the Ce–O bond where Ce is present in the 3+ state. Finally, the higher energy level of the O (1s) signals located at 531.17 eV are due to OH on the surface and not related to the presence of either Ce$^{3+}$ or Ce$^{4+}$.

3.1.9 Thermogravimetric analysis

Thermogravimetric (TG) analysis was carried out to quantitatively analyze the presence of impurities and the stability of the nanostructure on its surface level. Samples were interfaced up to 850°C at a rate of 5°C min under nitrogen atmosphere and the resulting thermogram is shown in Fig. 3.9. In the sample Ce$_2$/Cd$_1$ had a weight loss of 10% as observed up to 850°C. This small reduction in the weight may be due to the removal of hydroxyl group. The weight loss is taken in two parts. (1) The reduction in weight loss is 3% as observed from room temperature to 200°C due to the release of physically adsorbed water and the water of crystallization from the catalyst’s surface. (2) A weight loss of 6% was as observed in TG curve in the temperature range of 200°C–500°C, due to solid phase transition or the removal of internal water molecule. The weight loss from 500°C to 850°C is due to the loss of mass but is very slight. Similarly, the weight loss in the sample Ce$_1$/Cd$_1$

![FIGURE 3.9](image_url) TG/DTA curve of CeO$_2$/CdO nanostructures in ratios Ce$_1$/Cd$_1$ and Ce$_2$/Cd$_1$. 
is 6% as observed up to 200°C and is due to the release of more surface water molecules. The weight loss of nearly 3% from 200°C to 500°C is due to the removal of chemically combined water molecules. The weight loss is less above 500°C as observed in TG curve. Both the samples are also highly stable on further heating. This confirms that cerium oxide and cadmium oxide are well dispersed with good average crystallite size [67,68].

The differential thermal analysis (DTA) curves of the two CeO$_2$/CdO nanostructures prepared in ratios 1:1 and 2:1 (Fig. 3.9) differ slightly. The nanostructure (Ce$_2$/Cd$_1$) exhibited three endothermic peaks. The first peak is in the range of 70°C–100°C with the minimum value at 85°C. The second endothermic peak is in the range of 151°C–214°C with its minimum value located at 178°C. The third endothermic peak is relatively broad in the range of 273°C–362°C with its minimum at 336°C. Likewise, the sample Ce$_1$/Cd$_1$ exhibited three endothermic peaks. The first endothermic peak is broad and in the range of 63°C–113°C with the minimum of 85°C. The second endothermic peak is in the range of 148°C–204°C with a minimum at 180°C. The third endothermic peak is in the range of 293°C–336°C with a minimum at 311°C. The weight loss is probably due to the removal of physically adsorbed water and interstitially combined H$_2$O molecules. The weak peak at 400°C–850°C indicates the transformation of the CeO$_2$ and CdO oxides phases [69]. The DTA curve did not show the exothermic peak related to crystallization, also indicating the formation of CeO$_2$/CdO nanostructures.

### 3.1.10 Photocatalytic activity

The photocatalytic activity of the binary metal oxides was evaluated by taking RhB as the model pollutant. Degradation studies were carried out at both UV light (365 nm) and visible light irradiation. The process conditions were optimized in terms of the following reaction variables:

1. effect of irradiation time on the photodegradation of RhB;
2. effect of pH on the photodegradation of RhB;
3. effect of initial concentration of RhB;
4. effect of catalyst dose;
5. reusability of catalysts; and
6. effect of catalyst on industrial wastewater.

### 3.1.11 Degradation of Rhodamine-B using CeO$_2$/CdO heterogeneous catalyst

In this investigation, we chose textile synthetic dye Rhodamine-B as a pollutant due to its high stability. Decomposition was examined using UV light irradiation as shown in Fig. 3.10A–D. The degradation capacity of all the samples with the ratios 1:0, 1:1, 1:2, 2:1, and 0:1 was investigated. The absorption
spectrum for decolorization of Rhodamine-B dye with and without CeO$_2$/CdO heterogeneous catalyst was recorded with time ($t$) in minutes under UV/visible light irradiation. The absorption peaks at 554 nm were observed for Rhodamine-B, confirming the photodegradation process [70]. The ratios between $C_t$ (concentration of dye at different time intervals of UV exposure) and $C_o$ (initial concentration) of the dye were plotted against the time of UV exposure, to compare the efficiency of the degradation under different conditions. The PCD efficiency of the different ratio samples
shows the following order 2:1 = 1:1 > 1:0 > 1:2 > 0:1. It was observed that the Ce$_2$/Cd$_1$ and Ce$_1$/Cd$_1$ samples exhibit the best photocatalytic activity compared to all other samples. Both the catalysts have better specific surface area, more reactive sites, mesoporous, higher ability toward absorption of light, and smaller size with high dispersion usually leading to better photodegradation and these features are present in CeO$_2$/CdO heterogeneous catalyst [71].

3.1.12 Photocatalytic degradation of Rhodamine-B dye using CeO$_2$/CdO heterogeneous catalyst (Ce$_2$/Cd$_1$ ratio)

The PCD activity of the CeO$_2$/CdO nanostructures was evaluated by decomposition of Rhodamine-B (10 ppm) using 50 mg of photocatalyst. The aqueous solution of the Rhodamine-B synthetic dye was not degraded in the absence of CeO$_2$/CdO heterogeneous catalyst under UV radiation. But the degradation of Rhodamine-B synthetic dye can be achieved efficiently at 365 nm using CeO$_2$/CdO dispersions in aqueous medium [72]. The photocatalytic activity was examined against the Rhodamine-B (RhB 99.95% purity). The aqueous Rhodamine-B solution (100 mL) containing 50 mg catalyst was stirred for 30 min, kept in dark conditions to reach the adsorption/desorption equilibrium between the catalyst and RhB molecules, then placed inside the reactor setup and subjected to irradiation by a UV light source ($\lambda_{\text{max}} = 365$ nm) to induce photochemical reaction; in this process, air was continuously bubbled into the reactor tube. At the end, the dye solution was completely degraded with the color change from pink color solution to colorless solution [73]. The degradation of Rhodamine-B values were calculated as follows: the PCD efficiency ($\eta$) of decolorization was calculated using the expression $\eta = (((C_o - C_t)/C_o) \times 100$, where $C_o$ is the initial concentration of Rhodamine-B and $C_t$ is the concentration of Rhodamine-B after time “t.” By using the above formula, the irradiation time (vs) percentage of degradation at different pH values was plotted as shown in Fig. 3.10D.

As can be seen, the degradation percentage increases with time. Degradation of RhB was carried out with catalyst after 210 min of irradiation time at pH 3.0, pH 7.0, pH 9.0, and only H$_2$O$_2$, and the dye degradation efficiency was 45%, 48.6%, 52%, and 22.1%, respectively. The percentage of degradation of dye was found to be less in neutral and acidic medium but maximum at pH 9.0. Because at the basic medium the generation of hydroxide (OH) radical is favored and increases the decomposition of the dye compared to pH 7.0. The results of the PCD spectra of RhB dye evidently prove the gradual decrease in the absorbance with increasing irradiation time, whereas the efficiency of dye degradation was 98.2%, 95.7%, and 92% for
RhB dye using the catalyst and H₂O₂ at pH 9.0, pH 7.0, and pH 3.0 in Fig. 3.10E. The results showed that the RhB dye was degraded at 150 min of irradiation time in basic medium whereas in neutral and acidic medium, the dye was degraded after 240 and 270 min, respectively.

The photocatalytic activities of the synthesized heterostructured sample depend on agitation speed, temperature, pH, and ionic strength. The generation of reactive oxygen species (ROS) in the presence of UV light by the catalyst is higher, which is responsible for the decomposition of dyes into small fractions [74]. The possible reason may be that in alkaline medium the hydroxide ion is more easily oxidized to hydroxyl radicals and thus the efficiency of the decomposition of dye is logically increased at pH 9.0. Hence, pH and H₂O₂ have more effects on the dye degradation. The concentration of *OH radicals in the whole system increases by the addition of H₂O₂ with the heterogeneous system. H₂O₂ is a better electron acceptor, since it generates more *OH radicals and inhibits the exciton recombination process at the same time. When H₂O₂ was added to the catalyst solution in basic medium, the maximum degradation was achieved in the first 150 min. Once degradation is completed, the next set of molecules can diffuse immediately on the surface of the catalyst for further degradation [75]. The O₂* and OH* radicals [ROS] can attack the functional group of the dye, which is attached to the surface of the catalysts through Coulomb interactions, and degrade the dye to the final products, such as CO₂, NO₃⁻, H₂O, and H⁺. Since RhB dye is a cationic dye, the decomposition is higher in basic media than in acidic and neutral media, which is related to the adsorption capacity of dyes on the surface of the catalyst.

3.1.13 Visible light–induced decomposition of Rhodamine-B using CeO₂/CdO heterogeneous catalyst (Ce₂/Cd₁)

To evaluate the photocatalytic activities of the synthesized CeO₂/CdO heterogeneous catalyst (2:1), visible light irradiation was used for the decomposition of well-known organic dye RhB. The absorbance spectrum of RhB synthetic dye is presented in Fig. 3.11. The degradation of RhB (10 ppm) was examined in the presence of 50 mg of catalyst—hydrogen peroxide by irradiating visible light at pH 9. The absorption at 554 nm decreases evenly for the decomposition of RhB dye. The pink RhB dye solution becoming colorless in the presence of catalyst is confirmed from the absorption spectra, which are significantly decreased at 554 nm with increase in visible light exposure time (min). The efficiency of the decomposition of dye was found to be 98%, which takes place after 40 min of irradiation of visible light in the presence of synthesized CeO₂/CdO heterogeneous catalyst. Finally, the results clearly indicate that the synthesized CeO₂/CdO heterogeneous catalyst has significant catalytic activity and hence this could be a beneficial photocatalyst for the decomposition of colored dyes.
3.1.14 Effect of pH on the photodegradation of Rhodamine-B dye

The rate of decomposition of Rhodamine-B synthetic dye was evaluated at different pH as shown in Fig. 3.10A—C. In acidic medium (pH 3), the concentration of hydronium ions are higher, proving a positive charge on the surface of the catalyst, as well as a decrease in the number of active sites on the surface of the CeO$_2$/CdO heterogeneous binary metal oxide catalyst. However, the substrate adsorbed on the surface of the catalyst, which directly affects the electron transfer between the excited state dye and CeO$_2$/CdO heterogeneous catalyst, further influences the rate of the reaction. The absorption of the cationic Rhodamine-B synthetic dyes in the mixture solution by CeO$_2$/CdO catalyst becomes poor in the acid medium because of lower concentration of active hydroxyl radicals and hence degradation of the structure of Rhodamine-B synthetic dye into smaller nontoxic molecules is still very slow. The rate of the decomposition process of the dye solution was found to increase along with higher pH value because the heterostructure binary metal oxide surfaces were predominantly negatively charged due to the presence of hydroxyl groups. With higher pH values, the formation of active *OH species is favored, which not only improves transfer of holes to the adsorbed hydroxyls, but also has electrostatic attractive effects between the negatively charged CeO$_2$/CdO heterogeneous catalyst particles and the operating cationic dyes [29]. Hence, we propose from our results that the surface of CeO$_2$/CdO is negatively charged so that the Rhodamine-B synthetic dye adsorbs on it through the ammonium groups that are positively charged.

In acidic medium

$$\text{CeO}_2 + \text{CdO} + H^+ + \text{RhB}^+ \rightarrow \text{CeO}_2 + \text{CdO} + H^+ + \text{RhB}^+ \text{(Electronic repulsion)}$$ (3.1)
In basic medium

\[
\text{CeO}_2 + \text{CdO} + \text{OH}^- + \text{RhB}^+ \rightarrow \text{CeO}_2 + \text{CdO} \\
+ \text{OH}^- \rightarrow \text{RhB}^+ \text{(electronic attraction)}
\]  

3.1.15 Effect of irradiation time on the photodegradation of Rhodamine-B dye

UV light plays a crucial role in the decomposition of Rhodamine-B synthetic dye. The heterostructured binary metal oxide nanomaterials show outstanding PCD with increase in irradiation time. The reason behind this may be due to excitation of valence electrons from the ground state of the metal oxide source to the excited state by illumination of UV light source, which leads to the formation of high energy photoelectron. These photogenerated electrons in the conduction band and the holes in the valence band produce hydroxyl radicals in the whole system, which leads to the decomposition of dye by color change from pink to colorless [76]. The photodegradation efficiency of synthesized nanomaterial with different time intervals was studied to investigate the effect of irradiation time on the photodegradation of Rhodamine-B synthetic dye. This degradation process was carried out at room temperature under UV light irradiation until the degradation process completed. From the above results, we can see that Rhodamine-B synthetic dye is decomposed, which is directly proportional to UV irradiation time as shown in Fig. 3.10A–D. When Rhodamine-B synthetic dye in the presence CdO decorated ceria nanomaterial was irradiated with the UV light at different time intervals, a gradual change in color from pink to colorless occurs, because the CdO decorated ceria nanomaterial decreases the electron/hole recombination effect, improves the charge separation efficiency, and pumps the photogenerated electron of ceria to create a ROS and thus an increase in the degradation of pollutant [77].

3.1.16 Effect of catalyst dose on the photodegradation of Rhodamine-B dye

To explore the effect of catalyst loading for the decomposition of RhB dye, a series of batch experiments was carried out with catalyst CeO$_2$/CdO heterogeneous binary metal oxide nanostructures, in which the loading of catalyst was varied between 40 and 70 mg, and in all the cases we kept dye concentration (10 ppm) and pH 9.0 as constant. The light intensity also remains the same. Fig. 3.12 shows that the decomposition reaction increases up to 50 mg of catalyst in 100 mL of the dye solution due to increase in the reactive sites on the catalyst, beyond which it shows that the degradation process is reduced, which may be due to the scattering of light and weakening in the
penetration of light in the solution for the reaction \[78\]. At higher amount of catalyst in the dye solution, the high energetic molecules get inactive by collision with fewer energy molecules and the turbidity of the solution medium becomes higher, which decreases the penetration of light, thereby leading to the decrease in the rate of the reaction. Also, the photocatalyst absorbs limited light and the surface area becomes less because of the nanostructure agglomeration at higher concentration of catalyst.

3.1.17 Effect of initial concentration of Rhodamine-B dye

PCD of RhB dye was studied for the various concentration of dye for 5, 10, 15, and 20 ppm to identify the effect of initial concentration of RhB synthetic dye. The obtained results are shown in Fig. 3.13 in which the efficiency of decomposition of RhB synthetic dye increases up to 98% for 10 ppm dye concentration and then decreases to 60% for the 15 ppm dye concentration \[79\]. This may be due to the higher number of dye molecules preferentially adsorbed on the surface of photocatalyst with increase in the dye molecules, whereas the generation of ROS radicals and light irradiation time remain constant. PCD efficiency decreases due to the fewer number of ROS radicals for the decomposition of dye. Also, the penetration of photons becomes poor in high concentration of dye \[80\]. This investigation reveals that the maximum strength of RhB synthetic dye decomposed by a catalyst dosage up to 10 ppm. To determine the stability of the catalyst, the reusability of the heterostructured binary metal oxide catalyst was examined by separation of the CeO\(_2\)/CdO material used. The filtered catalyst was washed with double deionized distilled water and dried at 120°C in an oven for 2 h; the dried catalyst was then used for the further degradation of dye. In each cycle CeO\(_2\)/CdO heterostructured binary metal oxide catalyst showed only
minimum changes in the efficiency of dye decomposition. From the result, we found that the degradation efficiency is reduced only by 4% at the end of the three cycles, thus indicating that the CeO$_2$/CdO heterogeneous binary metal oxide catalyst was highly stable.

### 3.1.18 Removal of Rhodamine-B from urban wastewater

To illustrate the ability of our synthesized CeO$_2$/CdO heterogeneous nanostucture, the adequate photocatalytic effect for RhB in real wastewater was studied. The PCD experiments were carried out in industrial wastewater by using CeO$_2$/CdO binary metal oxide catalyst. The industrial wastewater containing Rhodamine-B dye (100 mL) with 50 mg catalyst and H$_2$O$_2$ at pH 9 was placed inside the photocatalytic reactor setup and subjected to irradiation by a UV light source (\( \lambda_{\text{max}} = 365 \text{ nm} \)). The absorbance capacity was measured for industrial wastewater with increasing time intervals using a UV–visible spectrophotometer. The absorption value of RhB was decreased consistently (at 552 nm) due to the structural degradation of RhB molecules. From the plot of \( C_t / C_0 \) versus irradiation time for the PCD of industrial wastewater, the dye degradation efficiency in wastewater was 89% of RhB dye, which was degraded after 150 min of irradiation time, thus indicating that the potential use of these materials in real wastewater treatment applications. We conclude that the increase in Cd ion concentration on the crystal lattice of CeO$_2$ leads to the decrease in crystallite size and maximize the surface area, which is readily available for preferential adsorption of dye molecules over the catalyst surface. Therefore the dye molecules, which are readily adsorbed in the surface of catalyst, will undergo decomposition.
3.1.19 Mechanism of photocatalysis

Electrons and holes are created by illumination of UV light on CeO₂/CdO catalyst. The charge transportation processes of CeO₂/CdO nanostructure leads to UV light-driven photocatalytic decomposition of dye as shown in Fig. 3.14. After absorption of UV light, the electron in the valence band of both the binary metal oxide is energized and excited to conduction band, thereby resulting in the separation of electron-hole pairs on the surface of the CeO₂/CdO binary metal oxide NPs. The holes in the valence band are trapped by the H₂O to form active hydroxyl radicals (OH), which is the second strongest oxidant having an oxidation potential of 2.8 eV next to fluorine and holes form superoxides (O₂⁻, HO₂⁻). The photo excitation state of the semiconductor generates electrons in the conduction band, which reacts with oxygen molecule to form superoxide radical anions (O₂⁻). Usually the various organic dyes undergoing the PCD under UV light irradiation is attributed to their oxidation by the ROS, which have an ability to oxidize the organic pollutant and yielding H₂O, CO₂ molecules. Our results show that CeO₂/CdO binary metal oxide nanostructures act as a good heterocatalysts toward the

![Schematic diagram of the charge separation of CeO₂/CdO nanostructures showing photogenerated electron transportation processes leading to UV light-driven photocatalytic degradation of dye.](image-url)
decomposition of RhB synthetic dye and the dye has a higher affinity toward the synthesized photocatalyst. Therefore due to the presence of synergic effects in between ultratine CeO$_2$/CdO binary metal oxide heterocatalysts lead to the decomposition of the various polluting organics. The complete photodegradation process can be summarized by the following reaction steps:

\[
\begin{align*}
\text{CeO}_2 + h\nu &\rightarrow \text{CeO}_2(e^- + h^+) \\
\text{CdO} + h\nu &\rightarrow \text{CdO}(e^- + h^+) \\
\text{CdO}(e^-) + \text{CeO}_2 &\rightarrow \text{CeO}_2(e^-) \\
e^- (\text{CB, CeO}_2) + O_2 &\rightarrow O_2^* \\
O_2^* + H_2O &\rightarrow HO^* \\
h^+ (v_B \text{ CdO}) + H_2O &\rightarrow \text{CdO} + H^+ + HO^* \\
\text{RhB} + (O_2^* + h^+ + HO^*) \text{ (ROS)} &\rightarrow \text{mineralized products} \rightarrow \text{CO}_2 \\
&\rightarrow H_2O
\end{align*}
\]

\[(3.3) \quad (3.4) \quad (3.5) \quad (3.6) \quad (3.7) \quad (3.8) \quad (3.9)\]

### 3.2 Conclusion

In this chapter we discussed well-dispersed cerium oxide/cadmium oxide binary metal oxide nanostructures synthesized using the hydrothermal method. The prepared nanostructures were characterized by various studies. The XRD pattern showed that the cerium oxide-cadmium oxide nanostructures were of cubic phase clusters. The morphology of the binary metal oxides was found to be spherical in shape by FESEM and HRTEM analysis. RhB dye was degraded nearly at 150 min of irradiation time in basic medium whereas in neutral and acidic medium, the dye was degraded after 240 and 270 min. The generation of ROS in the presence of UV/visible light by the catalyst was found to be higher, which is responsible for the decomposition of dyes into small fractions. The possible reason is because, in alkaline medium, the hydroxide ion is more easily oxidized to hydroxyl radicals and thus the efficiency of the decomposition of dye is logically increased at pH 9. Hence, pH and H$_2$O$_2$ have more effects on dye degradation. The synthesized nanostructures can be used as an anticancer agent. The different oxidation states of metal oxides can tune the activities of the nanomaterials.

### References


