Research Article

Visible Light Photocatalytic Activity of CeO_2 - ZnO - TiO_2 Composites for the Degradation of Rhodamine B

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TiO_2 plays a significant role in many applications including solar cell. Consecutively to absorb the low-energy radiation, it is very much essential to tune the optical property of TiO_2 . We fabricated CeO_2 - ZnO - TiO_2 semiconductor composites by sol-gel method and achieved the absorption of lower energy radiation. The prepared composites were characterized by TG-DTA, UV-DRS, XRD, AFM, TEM and FESEM techniques. The particle and crystalline size of the composites was calculated using FESEM and XRD techniques, respectively. The photocatalytic activity of the synthesized composite for the degradation of Rhodamine B (RhB) under visible light irradiation was investigated. The photocatalytic degradation of RhB under various experimental conditions such as amount of catalyst, initial dye concentration and H_2O_2 amount was also demonstrated and the rate constant was calculated using L-H model.

1. Introduction

Semiconductor metal oxide plays an important role in heterogeneous catalysis, electrochemistry, gas sensors, and other applications. Recently titanium dioxide (TiO_2) received a lot of attention due to its chemical stability, nontoxicity, and low cost. TiO_2 is used as a gas sensor, antireflection coating in many thin-film optical devices, biomaterials, catalyst/support/additive in catalytic reactions [1–4] and as a good photocatalyst [5, 6]. It is well known that TiO_2 absorbs wavelength shorter than 385 nm due to its band gap of about 3.2 eV. Since very narrow range of such high energy radiation is available in solar light spectrum, it is very difficult to convert solar energy to chemical oxidizing power. So, it is very urgent to tune the optical property of TiO_2 for utilizing a large fraction of the solar spectrum to realize the indoor applications of this material. For this reason, modification of TiO_2 is done by various strategies like coupling with a narrow band gap semiconductor, metal ion/nonmetal ion doping, codoping with two or more foreign ions, surface

sensitization by organic dyes or metal complexes, surface fluorination, and noble metal deposition. Nanocomposites such as TiO_2 - SiO_2 [7, 8], ZnO - CdS [9], TiO_2 - WO_3 [10, 11], TiO_2 - CeO_2 [12], TiO_2 - Fe_2O_3 [13], In_2O_3 - TiO_2 [14], TiO_2 - CdSe [15], TiO_2 - CdS [16], and TiO_2 - ZnO [17] have been considered as effective photocatalysts.

Cerium oxide (CeO_2) is the most reactive rare earth metal oxide that has broad range applications in various fields [18] and it is an additive in the automotive three-way catalysts [19]. The redox couple of $\text{Ce}^{3+}/\text{Ce}^{4+}$ and the high capacity to store oxygen of CeO_2 have gained additional importance in the application of heterogeneous catalysis. However the poor thermostability of pure CeO_2 has limited its application in oxygen storage [20, 21]. To overcome this problem, some strategies have been adopted like mixing with metal or metal oxide to increase the thermal stability. The mixing of two different metal oxides leads to not only the thermal stability but also the different physical and chemical property from the individual metal oxides. There are many reports available

on mixed metal oxides of CeO_2 - TiO_2 to improve the thermal stability of CeO_2 and increase the photocatalytic performance of TiO_2 [22–27].

ZnO has been reported to be photoactive for the degradation of phenol and nitrophenol though some photocorrosion effects in the liquid-solid phase [16]. Pure ZnO has high recombination rate of photogenerated electron-hole pair. This high recombination rate is considerably decreased by modification with noble metals, metal oxides, metal sulfides, transition metals, and other components [28–31]. Among the above, the noble metal of Ag deposition shows significant importance, since it effectively traps the photogenerated electrons and also the surface plasmon resonance effects create an extra local electric field to facilitate the electron-hole pair production and separation [32]. The electrochemical process and photocatalysis on ZnO/ TiO_2 electrode were studied and they are proven to be the best electrodes, which is due to the better absorption ability of ZnO/ TiO_2 film electrode.

In this work, we fabricated CeO_2 -ZnO- TiO_2 semiconductor composite by sol-gel method and calcinated it at 700 and 800°C for 5 hrs. The physicochemical properties of the composites were studied by TG-DTA, UV-DRS, XRD, AFM, and FESEM. The optical property was tuned by changing the stoichiometric amount of CeO_2 and calcination temperature and achieved longer wavelength adsorption in UV-Vis spectrum. The particle and crystalline size of the composites were calculated using FESEM and XRD techniques, respectively. The photocatalytic degradation of RhB under visible light irradiation using the composite catalysts was investigated under various experimental conditions and the rate constant was calculated using L-H model. To the best of our knowledge, this is the first report on synthesis and characterization of CeO_2 -ZnO- TiO_2 semiconductor composite.

2. Experimental

2.1. Materials. All chemicals used were of analytical grade and used as such without further purification. Double distilled water was used in all experiments.

2.2. Synthesis. The CeO_2 -ZnO- TiO_2 composites were prepared by sol-gel method as follows. TiO_2 (1 M) was taken in 100 mL of isopropyl alcohol then the appropriate amount of ZnO was added into it. The above mixture was added dropwise into 900 mL of distilled water which contains $\text{Ce}(\text{NO}_3)_3$ at pH 1.5 (adjusted with HCl). The reaction mixture was continuously stirred for 18 hrs at 60–80°C and the obtained colloid was dried to get the composites. The mole ratio of ZnO: CeO_2 was chosen to be 0.8:0.2 and 0.7:0.3 and the composites was calcinated at 700 and 800°C for 5 hrs separately. Based on the CeO_2 amount, the composites will be denoted as follows: CZT-A-1 (for 0.2 M of CeO_2 calcinated at 700°C), CZT-A-2 (for 0.2 M of CeO_2 calcinated at 800°C), CZT-B-1 (for 0.3 M of CeO_2 calcinated at 700°C), and CZT-B-2 (for 0.3 M of CeO_2 calcinated at 800°C).

2.3. Characterization. Thermogravimetry-differential thermal analysis (TG-DTA) of the as prepared sample was carried

FIGURE 1: Structure of RhB.

out using (TG/DTA) SII TG-DTA6200 instrument. UV-Vis diffuse reflectance spectra (UV-DRS) were recorded on Shimadzu UV-2450 Spectrophotometer equipped with an integrated sphere assembly and using BaSO_4 as a reference sample. The surface morphology of the composite was studied with HRTEM along with its SAED pattern images which were taken in TECNAI T20 high-resolution transmission electron microscopy (HRTEM) operating at 200 keV. Field emission scanning electron microscope (FESEM) images were taken using Carl Zeiss Σ IGMA instrument with the resolution of 1.2 nm. Surface topography of the composite was characterized by atomic force microscopy (AFM) using Park System AFM XE 100. Powder X-ray diffraction was conducted on a XPERT-PRO diffractometer using Cu $K\alpha$ radiation.

2.4. Photocatalytic Activity. The photocatalytic activity of the composites was investigated for the degradation of RhB (structure shown in Figure 1) under visible light irradiation. The photo reactor “Heber Visible Annular Type Photo reactor” (as shown in Figure 2) equipped with 300 W tungsten halogen lamp (8500 lumen) was used for the investigation. The photo reactor was comprised of a borosilicate immersion jacketed tube to hold the lamp with inlet and outlet for water circulation to cancel the IR radiation. The immersion well is held at the centre of a reaction chamber. The inner surface of reaction chamber is fitted with highly polished anodized aluminum reflector. In a typical process, aqueous suspension of RhB and composite was taken in a glass tube and unless stated otherwise 10 mmol of H_2O_2 is added. Prior to irradiation, the suspension was magnetically stirred in dark for 30 min to attain the adsorption-desorption equilibrium. At the given time interval 3.5 mL of the sample was withdrawn and centrifuged to separate the composite for analysis. The degradation of RhB was determined by measuring the absorbance at 554 nm on UV-Visible Spectrophotometer.

3. Results and Discussion

3.1. Characterization

3.1.1. Thermal Analysis. The as prepared sample of 0.2 M CeO_2 used was subjected to thermal analysis to determine

FIGURE 2: Schematic diagram of the photoreactor.

the desorption temperature of the various species. The TGA curve of the as prepared sample has three parts as shown in Figure 3. The first part below 100°C is attributed to the loss of adsorbed water on the surface. The second stage around 120 to 350°C may be due to the release of residual chemisorbed water and the release of organic residues. The third part appeared after 350°C ascribed to the removal of hydroxyl group on the materials. These results are well matched with the literature report [33]. The DTA curve in Figure 4 further confirms the loss of water and organic residues. The endothermic peak at around 40°C is attributed to desorption of water and isopropanol. The exothermic peak at 250°C confirms the release of residual chemisorbed water and the release of organic residues.

3.1.2. Crystallinity, Phase, and Structure. The phase and crystalline structure of the prepared composites were studied by XRD analysis and shown in Figure 5. The XRD pattern shows that the composites are in both anatase and rutile phases of TiO₂. The intensity of anatase TiO₂ peaks in the composite (at $2\theta = 25.38^\circ$ (101) and 48.08°) decreases, whereas the peaks at $2\theta = 27.42^\circ$ (110) and 54.58° belonging to the rutile form increase as the calcinations temperature increases from 700 to 800°C which was attributed to the formation of thermodynamically stable rutile phase. The percentage of anatase is given by $A (\%) = 100 / \{1 + 1.265(I_R/I_A)\}$, where I_A is the intensity of the anatase 101-peak at 25.38° and I_R is that of the rutile 110-peak at 27.42° . The calculated phase compositions in different composite catalyst are given in Table 1. The cubic structure of CeO₂ (JCPDS 81-0792) clearly appeared in the composite material. The intensity increases

FIGURE 3: TGA curve of the as prepared sample of CZT-A-1.

FIGURE 4: DTA curve of the as prepared sample of CZT-A-1.

FIGURE 5: XRD spectrum of the composites (where a: anatase, r: rutile, c: CeO₂, and z: ZnO).

TABLE 1: Percentage of phase composition, average crystalline size, and band gap energies of the composites.

Sample	Phase (%)		Average crystal size (nm)	Band gap energy (eV)
	Anatase	Rutile		
CZT-A-1	56.8	43.2	33.7	3.13
CZT-A-2	46.0	54	43.6	3.01
CZT-B-1	82	18	59.9	3.13
CZT-B-2	17.5	82.5	50.4	2.91

FIGURE 6: UV-Vis DRS spectrum of the composites.

may be due to the increase in the amount of CeO_2 in the composite. The ZnO pattern in the composite was well matched with the reported data JCPDS number 89-1397. The average crystallite size L can be estimated from the diffraction peaks using the Scherrer formula: $L = K\lambda/\beta\cos\theta$, where K is the shape factor (0.9), λ is the X-ray radiation wavelength ($1.54056 \text{ \AA}$ for $\text{Cu K}\alpha$), and β is the line width at half-maximum height of the main broadening. The crystal size of the composites was calculated and given in Table 1.

3.1.3. Optical Property. The optical property of the composites calcinated at different temperatures was investigated by UV-Vis diffused reflectance spectroscopy. The calcination temperature and amount of CeO_2 strongly influenced the absorption property of the materials as shown in Figure 6. The red shift was observed in the absorption spectrum on increasing the amount of CeO_2 . The calcinations temperature of 800°C made to strong absorption than that of 700°C . Since some of the $\text{Ce}^{4+/3+}$ sites can be replaced by Ti^{4+} ions, n-type impurity will be formed in CeO_2 lattice. Thus, the red shift in the absorption spectrum results from the charge transfer from impurity level to the conduction band of the TiO_2 and it agrees well with the literature report [34, 35]. The band gap energy of the composites was calculated using the formula $E_g = 1240/\lambda_g$, where E_g is band gap and λ_g is cutoff wavelength obtained by drawing tangent line in

the absorption spectrum as shown in Figure 6. The estimated band gap energies of the composites are given in Table 1.

3.1.4. Morphological Property. The morphology and microstructures of the composites were directly observed from the microscopic techniques. The FESEM images of the composites are shown in Figures 7(a) and 7(b) which reveals that CZT-A-1 is in spherical shape with average particle size of 132 nm and CZT-B-2 is in different shapes with average particle size of around 213 nm which are shown in Figure 7(b). The spherical shape of the composite CZT-A-1 is further confirmed by AFM technique as shown in Figure 7(c). The average particle size obtained from AFM image is 133 nm which is in good agreement with FESEM results. The three dimensional AFM image of CZT-A-1 is shown in Figure 7(d).

The HRTEM image of the composite CZT-A-1 is presented in Figure 7(e) which obviously proves the spherical particles of the composite and its average particle size of 128 nm. The highly magnified HRTEM image of the composite is shown in Figure 7(f). The SEAD pattern as shown in Figure 7(g) is attributed to the fact that the composite is in polycrystalline nature.

3.2. Photocatalytic Activity. Photocatalytic activity of the composites was investigated under visible light irradiation by choosing RhB as a model substrate. The time dependent absorption spectrum for the degradation of RhB by CZT-A-1 is shown in Figure 8. The photocatalytic activity at 0.2 g/L of catalysts amount and 5 mg/L of dye concentration was shown in Figure 9. The photocatalytic activity of the catalysts depends on the TiO_2 phase present in it. On increasing the percentage of rutile phase in the catalyst, the photocatalytic activity was decreased. The catalyst CZT-A-1 shows high photocatalytic activity as it contains high percentage of anatase phase of TiO_2 . Even though the band gap of the catalyst can be decreased from 3.13 to 3.01 eV and 3.13 to 2.91 eV by increasing the calcinations temperature and changing the amount of ZnO and CeO_2 , the photocatalytic activity cannot be increased because of phase transformation from anatase to rutile. The high calcinations temperature maybe leads to the formation of thermodynamically stable rutile phase in the composite.

3.2.1. Effect of Catalyst Amount. The amount of catalyst is a significant parameter in the photocatalytic degradation of organic dyes. To achieve high photocatalytic activity in optimum amount of catalyst, we have carried out a series

FIGURE 7: (a) FESEM image of CZT-A-1. (b) FESEM image of CZT-B-2. (c) One dimensional AFM image of CZT-A-1. (d) Three dimensional AFM image of CZT-A-1. (e) HRTEM image of CZT-A-1. (f) High magnification HRTEM image of CZT-A-1. (g) SEAD pattern of CZT-A-1.

FIGURE 8: The time dependent absorption spectrum for the degradation of RhB.

FIGURE 10: Degradation profile of RhB by varying the amount of CZT-A-1.

FIGURE 9: Degradation profile of RhB by different catalysts.

FIGURE 11: Degradation profile of RhB by varying the dye concentration.

of experiments by changing the amount of CZT-A-1 from 0.1 g/L to 0.5 g/L keeping the 5 mg/L of RhB and the percentage degradation profile was shown in Figure 10. The enhanced photocatalytic activity for 0.2 g/L catalyst amount was observed from 0.1 g/L. On further increasing the amount of catalyst, the photocatalytic activity is decreased. This may be due to the aggregation of catalyst in high concentration, which leads to reducing the absorption of light radiation by scattering effect [36]. So, the optimum amount of catalyst was found to be 0.2 g/L to achieve high efficiency; further experiments were carried out at this catalyst concentration.

3.2.2. Effect of Dye Concentration. Considering the dye concentration as one of the parameters in photocatalytic degradation, the photocatalytic activity will be decreased

after a certain dye concentration. To find out the effect of dye concentration for the degradation of RhB, a series of experiments was carried out by changing the RhB concentration from 5 mg/L to 20 mg/L and the results are shown in Figure 11. It is observed that, on increasing the RhB concentration beyond 5 mg/L, the degradation efficiency decreases. On increasing the amount of dye concentration, the amount of dye adsorbed on the surface of the catalyst also increases. This increasing of the adsorption may decrease the active sites of the catalyst to absorb the incident photons and then decreases the amount of formation of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ radicals. Thus, the photocatalytic activity of the catalyst decreases.

3.2.3. Effect of H_2O_2 Concentration. The photocatalytic degradation of a dye can be enhanced by increasing the

TABLE 2: Rate constant for the degradation of RhB.

Catalyst	Rate (min ⁻¹)	Amount of CZT-A-1 (mg)	Rate (min ⁻¹)	Dye Conc. (ppm)	Rate (min ⁻¹)	Amount of H ₂ O ₂ (mmol)	Rate (min ⁻¹)
CZT-A-1	0.0082	5	0.0031	5	0.0082	5	0.0029
CZT-A-2	9.865×10^{-4}	10	0.0082	10	0.0012	10	0.0082
CZT-B-1	0.0019	15	0.0027	15	9.83×10^{-4}	15	0.0031
CZT-B-2	0.0020	20	0.0024	20	3.87×10^{-4}	20	0.0021
		25	0.0027			25	0.0026

FIGURE 12: Degradation profile of RhB by varying the H₂O₂ amount.

concentration of active radicals of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$. Addition of H₂O₂ as a better electron acceptor can increase the hydroxyl radicals to degrade the RhB. On the other hand increased amount of hydroxyl radicals beyond the optimum amount will decrease the degradation efficiency by forming weak oxidant $\text{H}_2\text{O}^\cdot$ [37, 38]. In order to find out the optimum amount of H₂O₂ and to achieve high degradation rate, we have varied the amount of H₂O₂ addition from 5 mmol to 25 mmol keeping 0.2 g/L of CZT-A-1 and 5 mg/L of RhB. The photocatalytic efficiency increases from 5 to 10 mmol addition of H₂O₂ as shown in Figure 12. On further increase of H₂O₂ amount beyond 10 mmol, the degradation efficiency decreases; this may be due to the formation of weak oxidant $\text{H}_2\text{O}^\cdot$ [6]. Thus the optimum amount of H₂O₂ was found to be 10 mmol to achieve high degradation efficiency.

3.2.4. Kinetic Analysis. Photocatalytic degradation of many organic dyes follows a pseudo first order Langmuir-Hinshelwood kinetic model. The rate of the reaction is calculated by plotting $\ln(C_0/C)$ versus irradiation time using the following equation:

$$\ln\left(\frac{C_0}{C}\right) = k_{\text{app}}t, \quad (1)$$

where C_0 is the initial concentration of the dye solution (mol L⁻¹), C is the concentration of the dye solution at time t (mol L⁻¹), and k is the rate constant (min⁻¹).

The kinetic profiles for the degradation of RhB with different parameters and different catalysts are shown in Figures 13(a)–13(d) and the calculated rate constants are given in Table 2. The high degradation rate of 0.0082 min⁻¹ was observed by CZT-A-1 and the rate of the reaction is low for the other catalysts. This decrease in the rate may be due to the presence of rutile phase in high percentage. The rate constant increases from 0.0031 to 0.0082 min⁻¹ on increasing the amount of CZT-A-1 from 0.1 to 0.2 g/L. Further increasing the amount of catalyst shows detrimental effect. This same trend can be observed for varying the dye concentration and amount of H₂O₂.

3.2.5. Reaction Mechanism. When the catalyst is illuminated by the visible light, electron-hole pairs are created in conduction and valence band, respectively. The photogenerated electron-hole pair will migrate to the surface of the catalyst and react with the species adsorbed on the surface to form active radicals as given in the following equations:

Moreover, the photogenerated electron-hole pairs may recombine. The rate of electron-hole pair recombination can be decreased by adding electron acceptors; H₂O₂ is a better electron acceptor and inhibits the electron-hole recombination. Moreover, it will be photodecomposed to hydroxyl radicals as given in the equation below [6]. These hydroxyl radicals will decompose the organic dyes into CO₂ and water which is represented in

The high concentration of hydroxyl radical will lead to forming weak oxidant $\text{HO}_2^\cdot$ and then this weak oxidant will combine with hydroxyl radicals and forms molecular oxygen and water; on the other hand the higher hydroxyl radical will

FIGURE 13: (a) Kinetic profile for the degradation of RhB by different catalysts. (b) Kinetic profile for the degradation of RhB by varying the amount of CZT-A-1. (c) Kinetic profile for the degradation of RhB by varying the dye concentration. (d) Kinetic profile for the degradation of RhB by varying the amount of H_2O_2 .

combine itself and form peroxide molecule as given in the following formulas [37, 38]; this phenomenon may lead to decreasing the degradation efficiency:

4. Conclusion

We have fabricated CeO_2 - ZnO - TiO_2 semiconductor composite by sol-gel method and calcinated it at 700 and 800°C for 5 hrs. Physicochemical properties of the composites were

studied by TG-DTA, UV-DRS, XRD, AFM, and FESEM techniques. The optical property was tuned by changing the stoichiometric amount of CeO_2 and calcinations temperature and achieved longer wavelength adsorption in UV-Vis spectrum. The particle and crystalline size of the composites were calculated using FESEM and XRD techniques, respectively. The enhanced photocatalytic activity for the degradation of RhB under visible light irradiation was demonstrated. The highest photocatalytic activity was demonstrated on changing the essential parameters such as catalyst amount, dye concentration, and H_2O_2 amount. The first order rate constant for the degradation of RhB was calculated using L-H model. This photocatalytic study confirms that these composites can be utilized for solar light harvesting.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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