# In-Situ Synthesis of CeO<sub>2</sub>/ZnO Composite Nanoparticles and Its Application in Degradation of Rhodamine B Using Sonocatalytic & Photocatalytic Method

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**Abstract:** Individual CeO<sub>2</sub>, ZnO and bimetal oxide core shell CeO<sub>2</sub>/ZnO composite nanoparticles are synthesized without any stabilizers using in-situ precipitation technique. The structure, morphology and particle size of the synthesized nanoparticles were analyzed by using X-ray powder diffraction, scanning electron microscopy and Transmission electron microscopy. Results reveal that the phase structures of CeO<sub>2</sub>/ZnO are composited by cubic (fluorite) phase of CeO<sub>2</sub> and hexagonal (wurtzite) phase of ZnO. Structure characterization of core shell particles by Transmission electron microscopy indicates that the ZnO shell is around 5 nm in thickness and CeO<sub>2</sub> core is 9 nm in diameter. The effectiveness of the synthesized CeO<sub>2</sub>/ZnO used as catalysts for the photocatalytic well as sonocatalytic degradation of Rhodamine B dye has also been investigated. The results showed that Photocatalysis was more efficient than sonocatalysis in degradation of Rhodamine B.

**Keywords:** Chemical synthesis, catalytic properties, nanostrectures, transmission electron microscopy (TEM), X–Ray diffraction

#### 1. Introduction

Dyes contribute to a substantial proportion of the effluents of textile, paper, leather, cosmetics industries. When such effluents mix with water bodies during disposal, presence of dyes may lead to health hazards[1]. Dyes can be potentially carcinogenic and toxic in nature and hence, much attention has been given by researches to develop photocatalytic materials that degrade these dye contents [2].

Coating of an inorganic nano-sized material with another inorganic material to form core/shell type nanostructures has become an important route for synthesis of functional nanomaterials.

Cerium oxide is one of the most activity oxide catalysts in the rare earth oxide series and has high oxygen storage capacity, redox properties, and metal support interactions [3].  $CeO_2$  is however, generally not considered as photoactive material [4]. Esch et al, studied about the electron localization of  $CeO_2$  with precise observation of high-resolution scanning tunneling microscopy, reveals that the defects of  $CeO_2$  are difficult to move. The results are indicative of the inactive photo properties of  $CeO_2$  [5]. Lin et al reported in their earlier work that in order to improve activity of  $CeO_2$  nanoparticles,  $CeO_2$  nanoparticles have been doped with 3d transition metal ions in bulk, but it has not improved the activity of  $CeO_2$  nanoparticles to a remarkable extent.

ZnO is a semiconducting material with a wide and direct band gap. Because of their photocatalytic activity, low cost and environmental sustainability, ZnO based materials find application in many fields [6]. ZnO being an important semiconductor catalyst, we intend to synthesize core/shell-type  $CeO_2/ZnO$  nanoparticles, where ZnO couples with  $CeO_2$  in structure and energy band; and can take cooperative effects, to enhance the catalytic activity of  $CeO_2$ .  $CeO_2$ -based composites have been studied largely, for instance,  $CeO_2/ZnO$  composite materials have been studied for the higher efficient photocatalyst and UV filters [7].

CeO<sub>2</sub>/ZnO composites have been reported to be synthesized via various methods, such as atmospheric pressure metal-organic chemical vapor deposition (AP-MOCVD) [8], hydrothermal synthesis [9], the soft solution chemical route [10], the solid-stabilized emulsion route [11], the sol-gel method [12] and the precipitation technique [13]. The Precipitation method of synthesis is simple, cost-efficient, allows the fabrication of products on a large industrial scale and it provides reproducible results.

However, photocatalysis has still not gained acceptance as an adequately efficient and effective and alone technology for the commercial level decontamination of waste water[14]. Recently, Ultrasonic (US) irradiation mediated by suitable catalysts(sonocatalysis) has been receiving attention as a promising technique for the treatment of hazardous organic pollutants in wastewater[15]-[17]. However the degradation rate is slow compared to other established methods [18].

This study uses a precipitation route, to carry out synthesis of  $CeO_2$ , ZnO and in-situ synthesis of  $CeO_2/ZnO$  core/shell nanoparticles. The nanoparticles are characterized using XRD, SEM and TEM measurement and their photocatalytic activity in the degradation of RhB dye is studied.

#### 2. Experimental Procedure

#### 2.1. Materials

Cerium Nitrate hexahydrate and Zinc Acetate dihydrate precursors were obtained from S. D. Fine Chemicals Ltd., Mumbai, India. Sodium hydroxide was obtained from Merck Ltd., Mumbai, India. Rhodamine B (RhB) dye was procured from Shah Enterprises, India. Deionized water was used for all dilution and sample preparation.

#### 2.2. Synthesis of CeO<sub>2</sub>/ZnO Core Shell Composite Nanoparticles

The synthesis of core/shell type  $CeO_2/ZnO$  nanoparticles via precipitation method, proceeded as follows. In a typical procedure, 1.5 g (0.1 gmol) of  $Ce(NO_3)_2$ .  $6H_2O$  was dissolved in 50 ml of deionized water–ethanol matrix (equal volumes) and 0.6 g, (0.3 gmol) sodium hydroxide was also dissolved in 50 ml of deionized water–ethanol matrix were mixed drop wise. The reaction was allowed to proceed for 4 hrs at  $35 \pm 2^{\circ}C$ . To this solution, 2.2 g (0.2 mol) of  $Zn(CH_3COO)_2 \cdot 2H_2O$  in 50 mL of deionized water–ethanol matrix (equal volumes) was added drop wise, stirring was continued for 10 more minutes. An equal molar amount of sodium hydroxide in another deionized water–ethanol matrix was prepared and added to the above colloidal solution drop by drop with continuous stirring at 80°C. The reaction was allowed to proceed for 1hr while maintaining the temperature. The resulting solution was centrifuged at 10,000 rpm for 10 minutes to separate the product, and the settled product was washed several times with deionized water and ethanol to remove the byproducts. After complete washing, the product was dried in a hot air oven at 120°C for 3 hrs.

#### 2.3. Characterization

The phase structures of CeO<sub>2</sub>, ZnO, and CeO<sub>2</sub>/ZnO core shell nanoparticles were studied on a Rigaku Mini-Flex X-Ray Diffractometer instrument using Cu K $\alpha$  radiation source ( $\lambda$ =0.154 nm). XRD patterns were recorded at angles between 20° and 80°, with a scan rate of 2°/min. Particle sizes were determined using the Debye–Scherrer equation. Sample preparation for Scanning Electron Microscopy (SEM) includes the deposition of platinum on powder of the composite particle. The morphology and diameter of individual CeO<sub>2</sub>

and ZnO nanoparticles were characterized by a JEOL, JSM-6380 LA 15KV Scanning electron microscope. The morphology of core/shell CeO<sub>2</sub>/ZnO nanoparticles, and diameter of core and thickness of 0shell were characterized by Philips Model CM200 Transmission Electron Microscope having operating voltage from 20kv to 200kv with the resolution of 2.4  $A^0$ . The photocatalytic and sonocatalytic degradation of RhB dye, using the synthesized particles as catalysts, was investigated using a Perkin–Elmer UV-visible Spectrophotometer. Demineralized water was used as a blank reference.

# 2.4. Photocatalytic Degradation Experiment

The photoreactor is a closed box with a UV lamp Spectroline XX-15 N that emits radiation at 365 nm with intensity of 2000 W/cm<sup>2</sup>. The solution of RhB was made at 25 ppm concentration each, in order to compare the activity of the composite CeO<sub>2</sub>/ZnO composite nanoparticle photocatalyst with the photocatalytic activity of individual CeO<sub>2</sub> and ZnO nanoparticle photocatalysts. Solutions with 50 mg of CeO<sub>2</sub>, ZnO and CeO<sub>2</sub>/ZnO core/shell photocatalysts suspended in 100 ml dye solution were prepared to make 0.05% aqueous solution. The suspension was subjected to irradiation under UV-vis light for a span of 90 minutes. Prior to photoreaction, the suspension was magnetically stirred in dark condition for 30 min to establish absorption/desorption equilibrium condition. Also during the photocatalytic reaction, the aqueous suspension was magnetically stirred. The solutions were exposed to ambient temperature of 35°C and pH of 7 was maintained during the process. Aliquots of mixture were taken out with the help of a syringe at periodic intervals during the irradiation, using a micropipette. These samples were subjected to an ultracentrifuge in order to separate any suspended solids and then analyzed in the double beam UV-vis spectrophotometer. The wavelength of maximum absorbance ( $\lambda$ max) of dye was found to be 554 nm for RhB dye. Reproducibility of the obtained experimental data is very important in investigation related to the effects of the operating parameters.

## 2.5. Sonocatalytic Degradation Experiment

Sonocatalytic degradation process of Rhodamine B was carried out in a glass reactor filled with 100 ml of aqueous dye solution at a concentration of 25 mg/L. The experiments performed with different addition amounts showed that the sonocatalytic degradation ratios of Rhodamine B tempestuously increase with the increase of nano-sized catalyst powder up to 0.05% and then the degradation ratio of Rhodamine B reached a constant value for any additional amount of catalyst. A constant concentration of sonocatalyst at 0.05% was hence maintained during the degra dation experiment. The suspension was magnetically stirred in dark condition for 30 min to establish absorption/desorption equilibrium condition. The solutions were exposed to ambient temperature of 35°C and pH of 7 was maintained during the process. Ultrasonic irradiation was achieved by means of an ultrasonic bath (Dakshin Ultrasonic Model 9L 300 H/DF), which was operated at a frequency of 20 kHz and an effective power output of 80 W through manual adjusting. Under these mild ultrasonic conditions, degradation of organic substances due to ultrasound is generally reported to be quite low [19]·

#### 3. Results and Discussions

#### 3.1. X-Ray Diffraction (XRD)

The phase identification and structural changes were investigated with the help of X ray diffraction (XRD) technique. Fig. 1 depicts the typical XRD patterns recorded over  $20^{\circ}-80^{\circ}$  for the individual as well as CeO<sub>2</sub>/ZnO composite nanoparticles. It is seen that there are two sets of diffraction peaks for the CeO<sub>2</sub>/ZnO sample, which indicates that the as-synthesized samples are composite materials. The XRD peaks at  $20^{\circ}$  28.541° (111), 33.071°(200), 47.471°(220), 56.331°(311), 59.071°(222) and 69.401°(400) are attributable to CeO<sub>2</sub> as shown in Fig. 1. However, the pure CeO<sub>2</sub> has peaks of a weaker intensity than CeO<sub>2</sub>/ZnO peaks

(Fig.1b). According to the Debye-Scherrer formula, the strongest peak (111) at  $2\theta = 28.575^{\circ}$ , the peak (200) at  $2\theta = 33.139^{\circ}$ , the peak (220) at  $2\theta = 47.572^{\circ}$  and the peak (311) at  $2\theta = 56.402^{\circ}$  were used to calculate the average crystal size of the CeO<sub>2</sub> nanoparticles, which was determined to be around 13 nm. These diffraction peaks are identified as that of pure CeO<sub>2</sub> with a cubic phase, which is consistent with (JCPDS Card No.: 34-0394)



Fig. 1. XRD plot of CeO<sub>2</sub>, ZnO, CeO<sub>2</sub>/ZnO nanoparticles.

It was observed that ZnO synthesized samples have indeed diffraction peaks of ZnO with 2 $\theta$  at 31.86° (100), 34.54° (002), 36.32° (101), 47.62° (102), 56.66° (110), 62.96° (103), 68.04° (112), and 69.18° (201). All these diffraction peaks are indexed to hexagonal wurtzite ZnO structure & diffraction data were in good agreement with the (JCPDS card no. 36-1451). The average crystal size of ZnO is determined using Scherrer relation and it was found to be around 36 nm. Presence of any other peak was not observed, which attributes that no other phase is present in core shell composite nanoparticles. Peak positions for both CeO<sub>2</sub> and ZnO in the XRD patterns have no obvious shift comparing with their standard patterns. Therefore, the oxides of ZnO and CeO<sub>2</sub> should form a composite. Table 1 summarizes the crystal sizes and % crystallinity observed in individual as well as composite core/shell particles by X Ray diffraction.

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	Sr No	Particle	Average Crystal Size <i>d</i> nm	Average % Crystallinity
	1	CeO <sub>2</sub>	18	48.23
	2	ZnO	36	18.82
	3	CeO <sub>2</sub> /ZnO	26	24.25

Table 1. Average Crystal Size and % Crystallinity of CeO<sub>2</sub>, ZnO, CeO<sub>2</sub>/ZnO Composite Nanoparticles

# 3.2. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was carried out to provide evidence to the topological effect of the individual CeO<sub>2</sub> and ZnO as well as the CeO<sub>2</sub>/ZnO composite nanoparticles. The morphology, size and structure of the particles have been investigated in detail using SEM. Fig <sub>2</sub>, shows the SEM micrographs of the individual CeO<sub>2</sub> (Fig. 2a), ZnO (Fig. 2b) and CeO<sub>2</sub>/ZnO(Fig. 2c) nanoparticles respectively. The micrographs of the synthesized particle support the observations from the XRD patterns. SEM results were compared at the same magnification of 300X and 1000X. The agglomeration in the synthesized particles may be because of active surface charge present on the nanoparticles. The SEM image for CeO<sub>2</sub> attributes that the particles have smooth and sharp cuts, while for ZnO indicates that ZnO nanoparticles have an extremely rough surface. The rough surface morphology of the CeO<sub>2</sub>/ZnO nanoparticles as seen in the SEM image indicate that CeO<sub>2</sub> must have been coated with ZnO by which it impart rough surface morphology.







Fig. 2. SEM micrographs at 300X and 1000X magnifications respectively of a) CeO<sub>2</sub> b) ZnO c) CeO<sub>2</sub>/ZnO nanoparticles.

#### 3.3. Transmission Electron Microscopy (TEM)

Fig. 3 shows the TEM graphs of the  $CeO_2/ZnO$  core shell composite nanoparticle. The images clearly confirm the formation of  $CeO_2/ZnO$  composite nanoparticle, as proposed. The average size of particles as seen in the TEM graphs is in good agreement with the calculated crystallite size from XRD analysis. The dark grey or black coloured portions represent the  $CeO_2$  core, while the light grey color surrounding represents the ZnO shell. The particles were formed with a fairly narrow size distribution and uniform shape is observed. The average particle size was 14 nm with the average diameter of the  $CeO_2$  core being 9 nm and the average width of the ZnO coating being 4 nm. It can be clearly seen from the TEM image that the individual particles have aggregated to form secondary particles of larger size, as seen even in the SEM image (Fig. 2). The aggregation can be associated to the high surface energy of the nano particles due to presence of surface charge.



Fig. 3. TEM images and SAED pattern of CeO<sub>2</sub>/ZnO nanoparticles.

The select area electron diffraction (SAED) pattern corresponds to the synthesized  $CeO_2/ZnO$  nanoparticles (Fig. 3) Crystallinity could be observed based on the particles and their corresponding SAED patterns. The pattern supports the formation of a composite material with contribution from both  $CeO_2$  and ZnO evident in the image. The diffused ring patterns correspond to the presence of  $CeO_2$  while presence of crystalline ZnO is evident from more defined spots in the pattern.

#### 3.4. Photocatalytic Activity

Photocatalytic activity of  $CeO_2$ , ZnO and  $CeO_2/ZnO$  core/shell photocatalysts were evaluated through the degradation of a basic dye i.e. Rhodamine B in an aqueous solution under UV radiation, as mentioned in the degradation experiment. The removal of Rhodamine B in the presence of all three type of catalyst powders was confirmed by a drop in the absorbance peak within visible wavelength as shown in Fig. 4.



Fig. 4. UV-vis spectra of RhB during photocatalytic degradation.

It has been reported by Minero *et al* that when the alteration of the shape of the spectrum is not significant, it indicates that there is no colored degradation intermediates produced. Thus, the spectral interference during our reaction was negligible and the change in absorbance value can be due to dye degradation in presence of photocatalyst, after 90 mins. The concentration of Rhodamine B was detected at its maximum absorbance of 554 nm as found from the absorption peak in Fig. 4.

The degradation efficiency of Rhodamine B is defined as follows:

Degradation efficiency (%) = 
$$(C_0 - C_t)/C_0 \times 100\%$$
 (1)

where  $C_0$  is the initial concentration of Rhodamine B and  $C_t$  is the concentration of Rhodamine B at

reaction time t (min). Fig 5 depicts the degradation of rhodamine B in the presence of the synthesized core shell composite nanoparticles, under UV radiation at different time. It can be seen that the absorption peaks of rhodamine B solutions gradually decrease along with irradiation time, which indicates that rhodamine B in aqueous solutions is decomposed piece by piece under UV light.



Fig. 5. Degradation of RhB with respect to time in presence of photocatalyst.

The detailed degradation processes are shown in Fig. 6. It could be seen that the degradation ratio of Rhodamine B in the presence of nano-sized CeO<sub>2</sub> powder attains 36.56% within 90 minutes of exposure to UV light, while it was 65.20% for rhodamine B in presence of ZnO and 55.33% in presense of composite CeO<sub>2</sub>/ZnO nano-sized photocatalyst, respectively, at the same time. Correspondingly, the degradation ratio of rhodamine B in the absence of any catalyst under only UV irradiation, was only 7.05% at the same moment. These results indicate that the degradation effects of rhodamine B in the presence of nano-sized catalyst powders are significant than that of unanalyzed system.



Fig. 6. Effect of photocatalyst on degradation of RhB.

The increase in the degradation rate in the presence of catalyst can be attributed to the semiconducting nature of the catalyst particles. Irradiation of metal oxide particles with photons of energy equal to, or greater than their band gap energy, results in the promotion of an electron from the valence band (VB) to the

conduction band (CB) of the particle. The outcome of this process is a region of positive charged electron hole, in the valance band. The charge can migrate to the particle surface, where the holes can react with surface-bound hydroxyl groups (OH-) and adsorbed water molecules to form hydroxyl radicals (OH·) ie carry out water dissociation reaction. The high intensity of UV light generated in the reactor leads to generation of large amount of free radicals in the aqueous system, hence causing an increased degradation.

In addition, to infer the reaction kinetics of photocatalytic degradation of rhodamine B, the data of  $-\ln (C_t/C_0)$  for first-order reaction as a function of irradiation time (t) were calculated. In Fig. 7, the results indicate that all calculated values of  $-\ln (C_t/C_0)$  are approximately linear with the irradiation time all through for photocatalytic degradation of Rhodamine B for all cases; ie they conform to pseudo first-order kinetics reactions. Nevertheless, the rate constants of photodegradation processes of rhodamine B in presence of CeO<sub>2</sub>, ZnO and CeO<sub>2</sub>/ZnO composite particles are much larger than that of photodegradation of RhB solution without catalysts. This supports our intention for synthesis of photocatalytic materials for degradation of RhB dye.



Fig. 7. Influence of photocatalyst on rate of degradation of RhB.

The photocatalytic activities of these nanoparticles show significant differences. That is, the order of photocatalytic activities is  $ZnO > CeO_2/ZnO > CeO_2$ . The corresponding degradation ratios calculated are 65.20%, 55.33% and 36.56%, respectively, and that the degradation ratio under UV radiation alone is only 7.05%. The result confirms the intention of coating CeO<sub>2</sub> particles with more reactive ZnO, to increase its photocatalytic activity.

#### 3.5. Sonocatalytic Activity

Sonocatalytic activity of CeO<sub>2</sub>, ZnO and CeO<sub>2</sub>/ZnO core/shell sonocatalysts were evaluated through the degradation of a basic dye i.e. Rhodamine B in an aqueous solution under ultrasonic irradiation as mentioned in the degradation experiment. The removal of Rhodamine B in the presence of all three type of catalyst powders was confirmed by a drop in the absorbance peak within visible wavelength as shown in Fig. 8.

The degradation efficiency of Rhodamine B is defined as follows:

Degradation efficiency (%) = 
$$(C_0 - C_t)/C_0 \times 100\%$$
 (2)

where  $C_0$  is the initial concentration of Rhodamine B and Ct is the concentration of Rhodamine B at reaction time t(min). Fig 9 shows the comparison of degradation of rhodamine B in the presence of the synthesized nano-sized powders, under ultrasonic irradiation at different moments. It can be seen that the

absorption peaks of rhodamine B solutions gradually decrease along with irradiation time, which supports the investigation that Rhodamine B undergo chain scissning in presence of acoustic cavitation. However, as time progress it showed significant degradation.



Fig. 8. UV-vis spectra of RhB during sonocatalytic degradation.



Fig. 9. Degradation of RhB with respect to time in presence of sonocatalyst.

The detailed degradation processes are shown in Fig. 10. It could be seen that the degradation ratio of Rhodamine B in the presence of nano-sized CeO<sub>2</sub> powder attains 30.86% within 90 minutes of ultrasonic irradiation, while it was 55.81% for rhodamine B in presence of ZnO and 48.73% in presense of composite CeO<sub>2</sub>/ZnO nano-sized sonocatalyst, respectively, at the same time. Correspondingly, the degradation ratio of rhodamine B in the absence of any catalyst under only ultrasound irradiation was only 13.90% at the same moment. These results indicate that the degradation effects of rhodamine B in the presence of nanosized catalyst powders combining with ultrasonic irradiation are more aggressive than corresponding to those using only ultrasonic irradiation.

The increase in the degradation rate in the presence of catalyst can be attributed to the presence of solid particles in a liquid which increased the nucleation sites for cavity formation. Once undergoing electron shifts from the valence band to the conduction band, the metal oxide particles itself could also act as a catalyst to promote water dissociation reactions. The combined effects led to the generation of more free radicals in the

aqueous system, hence causing an increased degradation [20].



Fig. 10. Effect of sonocatalyst on degradation of RhB.

In addition, to infer the reaction kinetics of sonocatalytic degradation of rhodamine B, the data of  $-\ln (C_t/C_0)$  for first-order reaction as a function of irradiation time (t) were calculated. In Fig.11, the results indicate that all calculated values of  $-\ln (C_t/C_0)$  are approximately linear with the irradiation time all through for sonocatalytic degradation of Rhodamine B for all cases ie they conform to pseudo first-order kinetics reactions. Nevertheless, the rate constants of degradation processes for ultrasonic irradiation of rhodamine B in presence of CeO<sub>2</sub>, ZnO and CeO<sub>2</sub>/ZnO composite particles are much larger than that of RhB solution without catalysts. This supports our intention for synthesis of sonocatalytic materials for degradation of RhB dye.



Fig. 11. Influence of sonocatalyst on rate of degradation of RhB.

The sonocatalytic activities of these nanoparticles show significant differences. That is, the order of sonocatalytic activities is  $ZnO > CeO_2/ZnO > CeO_2$ . The corresponding degradation ratios calculated are 55.31 %, 48.73% and 30.86% respectively. And that the degradation ratio under ultrasonic irradiation alone is only 13.90% The results demonstrate that  $CeO_2/ZnO$  composite takes co-operative effects from individual components to demonstrate sonocatalytic activity at the used intensity and frequency of ultrasound. From investigations of photocatalytic & sonocatalytic degradation study of Rhodamine B. Photocatalytic showed higher degradation rate than that of sonocatalytic method.

# 4. Conclusion

Nano-sized CeO<sub>2</sub>, ZnO and Core-shell CeO<sub>2</sub>/ZnO composite nanoparticles were successfully synthesized by chemical precipitation method. CeO<sub>2</sub>/ZnO composite particles are composited of cubic (fluorite) form of CeO<sub>2</sub> and hexagonal (wurtzite) form of ZnO. The evidence of formation of CeO<sub>2</sub>/ZnO core/shell is given by the TEM image. Degradation characteristics of Rhodamine B confirm the inferior catalytic activity of CeO<sub>2</sub> nanoparticles in comparison to ZnO nanoparticles and thus support our intention of coating CeO<sub>2</sub> particles with a ZnO shell to increase the activity of CeO<sub>2</sub> as a photocatalyst.

# Appendix

Dye:

Common name	Rhodamine B
Class	Xanthenes
Solubility	Soluble
Empirical	C28H31ClN2O3
Structure	
Molecular weight	479.02
Лmax	554 nm

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