

Synthesis and Characterization of CeFeO₃ Photocatalyst Used in Photocatalytic Bleaching of Gentian Violet

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Ternary oxides have been used as effective photocatalyst for carrying out number of chemical reactions. Method of preparation has major effect on the performance of these mixed oxide catalysts. In the present work, cerium iron oxide catalyst was synthesized using co-precipitation method and specific heating cycle. Synthesized catalyst was characterized using X-ray diffraction patterns. Photocatalytic degradation on gentian violet dye was observed using this catalyst and progress of the reaction was monitored spectrophotometrically. The effect of variation of different parameters like concentration of gentian violet, pH, amount of semiconductor and light intensity was also studied. A tentative mechanism for the photocatalytic bleaching of gentian violet has been proposed.

Keywords: Photocatalysts, CeFeO₃, Photocatalytic bleaching, Gentian violet

INTRODUCTION

There are many methods for eliminating water pollutants like thermal dehydration, adsorption by charcoal *etc.* One of the most economical and ecofriendly methods is, however, the use of photocatalytic reactions. Following is a literature survey on the use of photocatalytic reactions in elimination of water pollutants.

Alton and Ferry used SiW₁₂O₄ as photocatalyst for the photocatalytic degradation of acid orange 7 [1]. Photoreduction of CO₂ and water into formaldehyde and methanol on aqueous suspension of SrTiO₃ and TiO₂ was investigated by Blajeni *et al.* [2]. Domen *et al.* studied photocatalytic decomposing of water vapors over NiO-SrTiO₃ catalyst [3]. Photocatalytic degradation of nitrobenzene with

combustion synthesized nano TiO₂ was investigated by Priya and Madras [4]. Photodegradation of dye pollutants on one dimensional TiO₂ nanoparticles under UV and visible irradiation was investigated by Chen *et al.* [5]. Wang *et al.* studied photocatalytic degradation and kinetics of orange-G using nano sized Sn(IV) TiO₂ as a photocatalyst [6].

Kako *et al.* have suggested some preventive method against catalytic poisoning of TiO₂ photocatalyst by H₂S [7]. Chittora *et al.* studied the photoreduction of CO₂ in presence of some photocatalyst like ZnO.Fe₂O₃ *etc.* [8]. Pt/CdS colloidal particles were used for photocatalytic hydrogen production from H₂S solution by Muradav *et al.* [9]. Swarnkar *et al.* observed the photocatalytic bleaching of gentian violet at CdS semiconductor surface [10]. Mansoori *et al.* used zinc oxide and lead oxide (PbO) as photocatalysts for the photocatalytic bleaching of rhodamine-B and rhodamine-6G [11,12].

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Photocatalytic degradation of azo dye acid readily in water using ZnO as photocatalytic has been investigated by Daheshvar *et al.* [13]. The photocatalytic bleaching of basic blue-24 in the presence of ZnO has been reported by Ameta *et al.* [14]. Kim *et al.* used ZnO coated TiO₂ nanoparticles for the flexible dye-sensitized solar cells [15]. Use of semiconducting iron(II) oxide in photocatalytic bleaching of some dyes (malachite green, crystal violet and methylene blue) has been reported by Ameta *et al.* [16]. Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins *et al.* [17]. The synthesis, characterization and photocatalytic activity of lanthanum cerium oxide (LaCeO₃) catalyst was reported by Jose *et al.* [18].

In present investigation, the semiconducting properties of a synthesized CeFeO₃ photocatalysts are utilized for photocatalytic bleaching of gentian violet. Like other inorganic semiconductor photocatalysts, CeFeO₃ also acts as an inorganic semiconductor. It absorbs photons to create electron-hole pair, which can subsequently participate in the redox reaction.

EXPERIMENTAL PROCEDURE

Materials and Methods

Gentian violet (CDH) as a modal dye and CeFeO₃ as a photocatalyst were used in this investigation. A stock solution of gentian violet (1.0×10^{-3} M) was prepared in doubly distilled water. The photocatalytic degradation of gentian violet was started by adding 0.10 g of CeFeO₃ to the dye solution. Irradiation was carried out keeping whole assembly exposed to a 200 W tungsten lamp (Philips, light intensity = 60.0 m W cm⁻²). This intensity of light at various distances from the lamp was measured with the help of solarimeter (SM CEL 201). The pH of the solution was measured by a digital pH meter (Systronics modal 335). The desired pH of the solution was adjusted by the addition of previously standardized sulfuric acid and sodium hydroxide solutions. The necessary condition for the correct measurement of optical density (O.D.) is that the solution must be free from semiconductor particles and impurity. The progress of photocatalytic reaction was followed by taking optical density at regular time intervals using an UV-Vis spectrophotometer (Systronics Modal 106).

Synthesis and Heat Treatment of Photocatalyst

CeFeO₃ was prepared by co-precipitation of metal nitrates upon addition of ammonium hydroxide. The methodology was as follows: 25 ml of 0.2 M aqueous solution of ferric nitrate was added to 25 ml of 0.2 M aqueous solution of (NH₄)₂Ce(NO₃)₆ to make the volume up to 100 ml. Then enough concentrated aqueous ammonium hydroxide was added rapidly to the mixture to adjust the pH of solution at 8.5.

The resulting precipitate along with the supernatant solution was kept in an oven at 110 °C for 15-16 h for drying of precipitate. Subsequently, stepwise calcinations were performed in a muffle furnace by heating the dried precipitate from 150 to 600 °C according to the heating schedule given in Table 1. The calcination at 600 °C was completed in four days 6 h heating everyday. After each heating, the material was furnace-cooled and ground in acetone with a pastel and mortar. The ground material was further heated in the next day and the procedure was repeated.

Table 1. Calcinations Temperature and Heating Schedule

| S. No. | Temperature | Duration (h) |
|--------|-------------|--------------|
| 1 | 150 | ½ h |
| 2 | 200 | ½ h |
| 3 | 225 | ½ h |
| 4 | 250 | ½ h |
| 5 | 300 | 1 h |
| 6 | 350 | 1 h |
| 7 | 400 | 2 h |
| 8 | 450 | 2 h |
| 9 | 500 | 3 h |
| 10 | 550 | 3 h |
| 11 | 600 | 24 h |

RESULTS AND DISCUSSION

The prepared ternary oxide was characterized by X-ray diffraction method and the results are shown in Fig. 1 and the corresponding characteristic XRD data are summarized in

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Table 2. The stoichiometry of the ternary oxide sample has been established with the help of published diffraction data file-JCPDS (Joint Committee on Power Diffraction

Standards).

Matching of mirror imaged XRD with XRD of CeFeO₃ from JCPDF file is shown in Fig. 2.

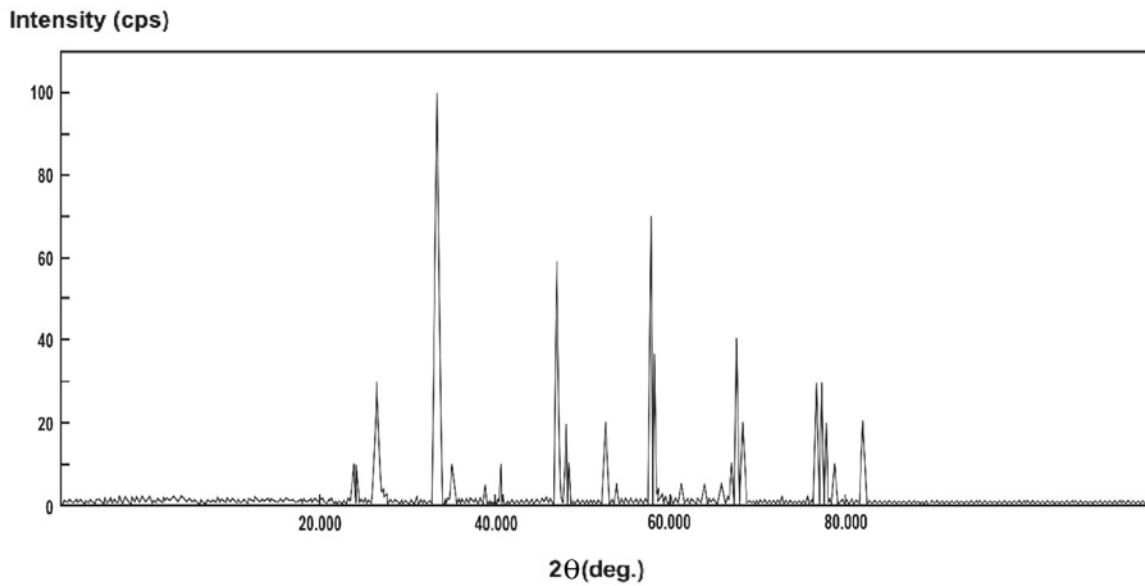


Fig. 1. X-ray diffraction pattern of CeFeO₃.

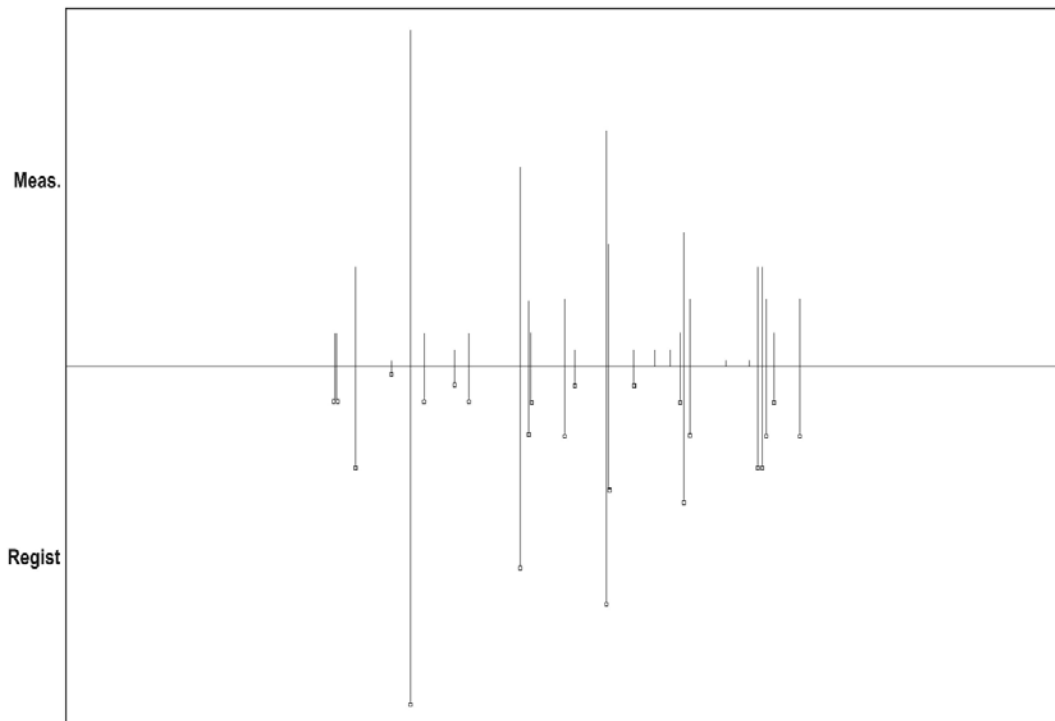


Fig. 2. Matching of mirror imaged XRD with XRD of CeFeO₃ from JCPDF file.

Table 2. XRD data of CeFeO₃

| S. No. | 2θ | D Value | Intensity | H k l |
|--------|--------|---------|-----------|-------|
| 1 | 22.065 | 3.930 | 10 | 110 |
| 2 | 22.723 | 3.910 | 10 | 2 |
| 3 | 25.353 | 3.510 | 30 | 111 |
| 4 | 32.290 | 2.770 | 100 | 112 |
| 5 | 34.140 | 2.624 | 10 | 21 |
| 6 | 38.048 | 2.363 | 5 | 211 |
| 7 | 39.854 | 2.260 | 10 | 202 |
| 8 | 46.507 | 1.951 | 60 | 4 |
| 9 | 47.672 | 1.906 | 20 | 221 |
| 10 | 47.832 | 1.900 | 10 | 23 |
| 11 | 52.290 | 1.748 | 20 | 114 |
| 12 | 53.544 | 1.710 | 5 | 311 |
| 13 | 57.594 | 1.599 | 70 | 24 |
| 14 | 57.673 | 1.597 | 30 | 204 |
| 15 | 61.161 | 1.514 | 5 | 231 |
| 16 | 67.084 | 1.394 | 10 | 40 |
| 17 | 67.578 | 1.385 | 40 | 224 |
| 18 | 68.363 | 1.371 | 20 | 41 |
| 19 | 77.024 | 1.237 | 30 | 116 |
| 20 | 77.618 | 1.229 | 30 | 43 |
| 21 | 78.147 | 1.222 | 20 | 225 |
| 22 | 79.073 | 1.210 | 10 | 234 |
| 23 | 82.432 | 1.169 | 20 | 135 |

Photocatalytic Degradation of GentianViolet

The photocatalytic degradation of gentian violet was followed at λ_{max} of 580 nm. The optical density-time data for a typical run are given in Table 3 and graphically presented in Fig. 3. It was observed that the optical density of gentian violet solution decrease in presence of semiconductor and light. The plot of $\log\text{OD}$ vs. time was leaner and hence, this reaction follows a pseudo first order kinetics. The rate constant for this reaction, as determined using the expression $k = 2.303 \times \text{slope}$, found to be $k = 1.02 \pm 0.026 \times 10^{-4} \text{ s}^{-1}$.

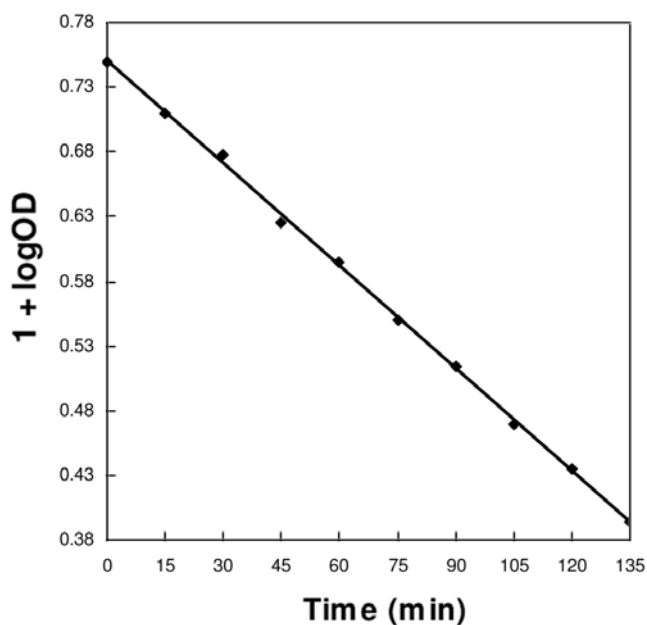
Effect of pH

The effect of pH on photocatalytic degradation was also investigated and the results are reported in Table 4. As seen, the rate of reaction increased with increasing of pH of solution

Table 3. A Typical Run. [Gentian violet] = $1.0 \times 10^{-5} \text{ M}$; pH = 6.0; Light intensity = 60.0 mW cm^{-2} ; CeFeO₃ = 0.10 g

| Time (min) | Optical density (O.D.) | 1 + logO.D. |
|------------|------------------------|-------------|
| 0 | 0.562 | 0.7497 |
| 15 | 0.513 | 0.7101 |
| 30 | 0.476 | 0.6776 |
| 45 | 0.422 | 0.6253 |
| 60 | 0.393 | 0.5944 |
| 75 | 0.355 | 0.5502 |
| 90 | 0.327 | 0.5145 |
| 105 | 0.295 | 0.4698 |
| 120 | 0.272 | 0.4346 |
| 135 | 0.248 | 0.3945 |

$$k = 1.02 \pm 0.026 \times 10^{-4} \text{ s}^{-1}.$$

**Fig. 3.** Plot of 1 + logOD vs. time for a typical run.

up to a pH of 6.0. However, a further increase in pH of solution resulted in decreased reaction rate. It may be explained on the basis that the surface of the semiconductor becomes negatively charged and the dye will remain in its neutral form, where it is electron rich due to the presence of

Table 4. Effect of pH. [Gentian Violet] = 1.0×10^{-5} M; Light Intensity = 60.0 mW cm⁻²; CeFeO₃ = 0.10 g

| pH | $k \times 10^4$ (s ⁻¹) |
|-----|------------------------------------|
| 4.0 | 0.57 |
| 4.5 | 0.60 |
| 5.0 | 0.69 |
| 5.5 | 0.73 |
| 6.0 | 1.02 |
| 6.5 | 0.90 |
| 7.0 | 0.83 |
| 7.5 | 0.73 |

Table 5. Effect of Concentration of Gentian Violet. pH = 6.0; Light Intensity = 60.0 mW cm⁻²; CeFeO₃ = 0.10 g

| [Gentian violet] $\times 10^5$ M | $k \times 10^4$ (s ⁻¹) |
|----------------------------------|------------------------------------|
| 0.4 | 0.80 |
| 0.6 | 0.85 |
| 0.8 | 0.96 |
| 1.0 | 1.02 |
| 1.2 | 0.96 |
| 1.4 | 0.92 |
| 1.6 | 0.82 |

Table 6. Effect of Amount of Semiconductor. [Gentian Violet] = 1.0×10^{-5} M; pH = 6.0; Light Intensity = 60.0 mW cm⁻²

| CeFeO ₃ (g) | $k \times 10^4$ (s ⁻¹) |
|------------------------|------------------------------------|
| 0.04 | 0.43 |
| 0.06 | 0.84 |
| 0.08 | 0.89 |
| 0.10 | 1.02 |
| 0.12 | 0.98 |
| 0.14 | 0.96 |
| 0.16 | 0.93 |

lone pairs on two nitrogen atoms. Therefore, these molecules will face a force of repulsion from negatively charged surface of the semiconductor; thus, resulting into a decrease in the rate of reaction.

Effect of Concentration of Gentian Violet

Effect of variation of dye concentration was also studied by taking different concentrations of gentian violet. The results are reported in Table 5. It is seen that the rate of photocatalytic bleaching increases with an increase in the concentration of the dye up to 1.0×10^{-5} M. It may be due to the fact that as the concentration of the gentian violet was increased, more dye molecules were available for excitation and energy transfer and, hence, an increase in the rate was observed. The rate of photocatalytic bleaching was found to decrease with further increase in the concentration of dye. This may be attributed to the fact that the dye will start acting as a filter for the incident light and it will not permit the desire light intensity to reach the semiconductor surface. Also, some dye aggregates may also form to retard the reaction rate.

Effect of Amount of Semiconductor

The effect of amount of semiconductor is also likely to affect the process of dye bleaching and therefore, different amounts of semiconductor were used. The results of this study are reported in Table 6.

It has been observed that, as the amount of semiconductor increases, the rate of photodegradation of gentian violet increases up to 0.10 g. A further increase in the amount of catalyst has no significant effect on the rate of reaction. This may be due to the fact that after a creation limit of 0.10 g, a further increase in CeFeO₃ will result in no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point above which any increase in the amount of semiconductor has negligible or no effect on the rate of photocatalytic bleaching of gentian violet, as any increase in the amount of semiconductor after this saturation point will only increase the thickness of the layer at the bottom of the vessel once covered by a photocatalyst. This was also supported by taking vessels of different dimensions.

Effect of Light Intensity

The effect of the variation of the light intensity on the rate was also investigated and the observations are reported in Table 7.

The data given in Table 7 indicate that the bleaching action is accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of

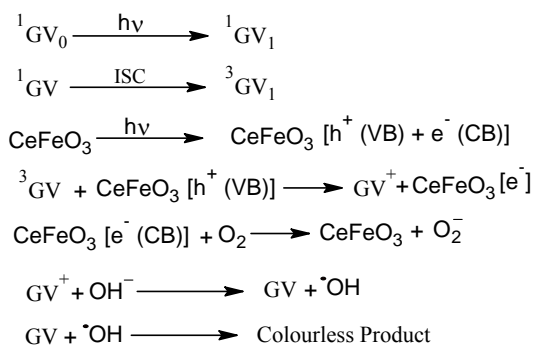
Table 7. Effect of Light Intensity. [Gentian Violet] = 1.0×10^{-5} M; pH = 6.0; Light Intensity = 60.0 mW cm^{-2} ; $\text{CeFeO}_3 = 0.10$ g

| Light intensity (mW cm^{-2}) | $k \times 10^4$ (s^{-1}) |
|--|-------------------------------------|
| 10 | 0.45 |
| 20 | 0.57 |
| 30 | 0.70 |
| 40 | 0.91 |
| 50 | 0.96 |
| 60 | 1.02 |

photons striking per unit area of the semiconductor powder. A linear behavior between light intensity and the rate of reaction was observed.

Mechanism

On the basis of experimental, a tentative mechanism for photocatalytic degradation of gentian violet may be proposed as:



Gentian violet (GV) absorbs radiations of suitable wavelength and goes to excited state. It then undergoes intersystem crossing (ISC) to the triplet state of the dye. This triplet state may donate its electrons to the semiconductor and the gentian violet becomes positively charged. The dissolved oxygen of the solution may pull an electron from the conduction band of semiconductor, thus regenerating the semiconductor and forming superoxide anion radical. The positively charged molecule of gentian violet will immediately react with hydroxyl ion to form $\cdot\text{OH}$ radicals and these $\cdot\text{OH}$

radicals will oxidize the gentian violet molecule into colorless product. The participation of $\cdot\text{OH}$ radicals as an active oxidizing species was confirmed by carrying out the reaction in the presence of a $\cdot\text{OH}$ radicals scavenger *e.g.*, 2-propanol, where the reaction rate was drastically retarded.

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