

Enhanced photocatalytic activity of Ce-doped ZnO nanopowders synthesized by combustion method

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Abstract: Facile and fast combustion method was used to synthesize ZnO and Ce-doped ZnO (CZO) nanocrystalline powders photocatalysts with different cerium concentrations (0.5 wt.%–10.0 wt.%) followed by calcination at 700 °C for 3 h. The prepared samples were characterized by a variety of characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) combined with energy dispersive X-ray diffraction (EDX), transmission electron microscopy (TEM), UV-visible spectroscopy, BET surface area analyser and photoluminescence spectroscopy (PL), to study the crystal structure, surface morphology, chemical composition and optical properties. It was observed from XRD results that synthesized powders had hexagonal wurtzite structure with the smallest crystallite size about 13 nm. Absorption spectra showed that cerium doping enhanced the light absorption properties towards the visible light region. Photoluminescence spectra for Ce-doped ZnO samples exhibited relatively weak near band edge (NBE) emission peaks as compared to that of pristine ZnO. The photocatalytic activities of the prepared samples were evaluated by photocatalytic degradation of Rhodamine B (RhB) under UV light and visible light ($\lambda \geq 420$ nm) irradiation. The textile mill effluent containing organic matters was also treated under sunlight using photocatalysis and the reduction in the chemical oxygen demand (COD) of the treated effluent revealed a complete destruction of the organic molecules along with colour removal. The results showed that the CZO photocatalyst doped with 3.0 wt.% cerium exhibited four times enhanced photocatalytic activity compared to pure ZnO. The enhanced photocatalytic activity could be attributed to extended visible light absorption and inhibition of the electron-hole pair's recombination.

Keywords: ZnO; cerium; combustion; photocatalyst; Rhodamine B; rare earths

There are many metal oxide semi conductive materials such as TiO₂ and ZnO which attracted the attention of researchers due to their unique photocatalytic capability in the degradation of toxic organic compounds present in global environment. Out of many semi conductive oxides TiO₂ and ZnO are opted as a most suitable candidate for vast applications in many industries, because these compounds are long term stable against corrosion, inert to chemicals, inexpensive and non-toxic^[1–5]. Amongst these, ZnO showed better performance as compared to TiO₂ in photodegradation of many toxic compounds^[6]. Therefore semi conductive ZnO has taken great attention of researchers to investigate its potential use in industrial applications. However, many problems remain unresolved in the ZnO photocatalyst system for practical applications, such as narrow spectrum response range and low separation probability of the photogenerated electron-hole pairs. Therefore, many techniques have been examined to extend the spectral response of ZnO into the visible region and to enhance its photocatalytic activity.

Doping with metallic cations or non-metallic anions has been widely used for the modification of ZnO to improve its photocatalytic activity or to extend its light absorption into visible region^[7–11]. It is known that metal ion doping can modify the surface properties of ZnO, hinder the recombination of photogenerated electron-hole pairs and increase the amount of the active sites. Especially, photocatalytic activity of ZnO can be significantly enhanced by doping with the lanthanide ions having 4f configuration^[12]. Among them, cerium doping has attracted more interest due to comparatively large ion which produces a localized charge perturbation during substitutional doping into ZnO lattice and increases its photocatalytic activity. Nowadays rare earth ion doped semiconductors have become more popular among researchers because of their unique optical properties and promising applications in optoelectronic devices^[13–19]. So many methods have been employed to produce pure ZnO nanopowders including hydrothermal, solvothermal, wet chemical etching, sol-gel and simple chemical combus-

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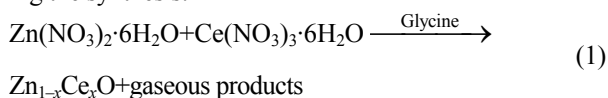
tion etc.^[20–25].

In this study 0, 0.5 wt.%, 1.0 wt.%, 2.0 wt.%, 3.0 wt.%, 5.0 wt.% and 10.0 wt.% Ce-doped ZnO (CZOs) photocatalysts were synthesized by using facile and fast combustion method. Combustion technique is not only inexpensive but also produces high quality products. The microstructure, morphology, chemical composition and optical properties of the photocatalyst changes by cerium doping, were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence (PL) emission spectra, BET surface area analyser and UV-vis diffuse reflectance spectra (DRS). The photocatalytic activity of all the prepared photocatalysts under UV as well as visible light illumination was evaluated by the degradation of RhB.

1 Experimental

1.1 Sample preparation

ZnO and Ce-doped ZnO (CZO) nanopowders were synthesized by combustion method similar to our previous report^[26], using zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), glycine ($\text{C}_2\text{H}_5\text{NO}_2$) as starting materials and cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) as doping source. Zinc nitrate and cerium nitrate acted as oxidant while glycine as fuel during the reaction. The fuel to oxidant molar ratio was adjusted to 1.7 as it exhibited enhanced photocatalytic activity during our previous study^[26]. In the combustion reaction, large amount of heat and non-toxic gases explosively evolved, resulting in dry, loose and voluminous nanocrystalline powders with high porosity. It was observed that the as-synthesized nanopowders were of brownish colour. While heat treatment in air at 700 °C for 3 h changed the colour to white. For simplicity, prepared Ce-doped ZnO samples with molar concentration of 0.5 wt.%, 1.0 wt.%, 2.0 wt.%, 3.0 wt.%, 5.0 wt.% and 10.0 wt.% were named as CZO-1, CZO-2, CZO-3, CZO-4, CZO-5 and CZO-6, respectively. The following chemical reaction occurs during the synthesis:



1.2 Characterization

Powder X-ray diffraction (XRD) patterns of as-synthesized ZnO and Ce-doped ZnO samples were recorded using a Rigaku Dmax-III A X-ray diffractometer with Ni filtered Cu K α radiation source at 40 kV and 30 mA. The average crystallite sizes were calculated by the Scherrer formula. The surface morphology, particle size and compositional analysis of photocatalysts were examined with a scanning electron microscope (Hitachi S-4800) combined with EDX and transmission electron micro-

scope (JEOL JEM 1200EX). Specific surface areas of samples were determined using a Brunauer Emmett Teller (BET) surface area analyzer (NOVA 2200e Quantachrome, USA) using nitrogen as a purge gas. UV-vis diffuse reflectance spectra (DRS) were measured in the range of 380–460 nm using a Hitachi U-4100 UV-vis spectrometer. The PL emission spectra were recorded using a Hitachi F-4500 fluorescence spectrophotometer. The samples excitation was made at 325 nm at room temperature.

1.3 Measurement of photocatalytic activity

The photocatalytic activity of ZnO and Ce-doped ZnO nanopowders were estimated by monitoring the degradation of RhB as a model compound in a self-assembled apparatus with a metal halogen lamp (HQIBT, 400 W/D, OSRAM, Germany) as the radiation source. In the present investigation, photocatalytic activities under visible as well as UV light were studied. The visible light ($\lambda \geq 420$ nm) used in the present study was obtained by using a filter with cut-off wavelength of 420 nm. The peak at 550 nm was used to monitor the photocatalytic degradation of RhB. For the photocatalytic experiment, 30 mg photocatalysts were suspended in RhB aqueous solution (30 mL) with a concentration of 15 mg/L in a beaker. The suspension was magnetically stirred for 30 min to reach the adsorption/desorption equilibration without light exposure. Following this, the photocatalytic reaction was started by the exposure of the desired light. The temperature of the suspension was kept at about 20 °C by an external cooling jacket with recycled water. After a setup exposure time, 3 mL suspension was sampled, centrifuged and the supernatant was taken out for UV-vis absorption spectrum measurement. The intensity of the main absorption peak of the RhB dye was referred to as the measure of the residual dye concentration.

1.4 Analytical method

The mineralization of substrate was measured by chemical oxygen demand (COD) reduction method. COD of textile effluent was estimated before and after the photocatalytic treatment with a standard dichromate method, using COD digester. As-received effluent was suitably diluted in order to facilitate light penetration through solution and the initial COD of diluted effluent was 307 mg/L. Amount of catalysts was 50 mg/25 mL and average intensity of sunlight was 1.22×10^5 lux during the photocatalytic measurements. The percentage photodegradation efficiency (η) was calculated from the following expression:

$$\eta = [(\text{COD}_{\text{initial}} - \text{COD}_{\text{final}}) / \text{COD}_{\text{initial}}] \times 100 \quad (2)$$

All the experiments were performed under the same experimental conditions such as sunlight irradiation (between 10 am and 4 pm), constant temperature, pH and photocatalyst load, etc.

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