

Synthesis and characterization of cerium–silver co-doped zinc oxide as a novel sunlight-driven photocatalyst for effective degradation of Reactive Red 120 dye

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ABSTRACT

Cerium–silver (Ce–Ag) co-doped ZnO was synthesized by precipitation–decomposition and tested for the degradation of Reactive Red 120 dye under natural sun light irradiation. Three weight percent Ce co-doped Ag–ZnO was found to be most efficient. Hence, this catalyst (3 wt% Ce–Ag–ZnO) has been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). XRD and XPS reveal the presence of metallic Ag and tetravalent Ce. Ag and Ce shift the absorption of ZnO to entire visible region. It was found that the Ce–Ag–ZnO exhibited higher degradation efficiency when compared to Ag–ZnO, Ce–ZnO, prepared ZnO, Commercial ZnO, TiO₂, and TiO₂-P25 at neutral pH (=7). Quantum yields of all processes were calculated and compared. Higher activity of Ce–Ag–ZnO in natural sunlight may be due to higher visible light absorption of Ce–Ag–ZnO when compared to native ZnO. The influences of operational parameters such as the amount of photocatalyst, dye concentration, initial pH on photo mineralization of RR 120 have been analyzed. The mineralization of RR 120 dye was confirmed by chemical oxygen demand (COD) measurements. A dual mechanism has been proposed for efficient degradation of RR 120 dye by Ce–Ag–ZnO under solar light at neutral pH. This photocatalyst was found to be reusable up to four runs.

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1. Introduction

Water is one of the basic requirements for the existence of life on earth. The availability of clean water is a major problem nowadays, and is expected to increase in the future due to the heavy global industrialization and increase in human population. Among many processes being proposed and/or developed for water purification, semiconductor mediated photocatalytic processing has received considerable attention. It is well-established that photocatalysis is an efficient method

to decompose the undesirable pollutants (toxic dyes, pesticides etc.) and to inactivate pathogens present in wastewater under solar or UV light [1–5]. However, UV light sources are generally expensive and not easy to obtain technologically for applications. In order to maintain the sustainable global development, exploring renewable energy with a minimal adverse environmental effect is necessary. Among the natural renewable energy sources sunlight can be used to excite a photosensitizer. An excited photosensitizer may then react directly with molecular oxygen, producing superoxide radical anion, and hydroxyl radicals etc., which can easily degrade organic molecules. Heterogeneous photocatalytic degradation of refractory organic pollutants from water by semiconductors has attracted extensive attention in the last decade [6–8]. TiO₂ and ZnO have been widely studied as efficient photocatalysts for the photodegradation of pollutants in wastewater owing to its inexpensiveness, strong oxidizing power, non-toxicity and

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long term photostability. However, the application of TiO₂ is limited under solar light because it absorbs only 3% of UV present in solar spectrum and it cannot efficiently utilize visible light [9,10]. It has been reported that ZnO has higher photocatalytic efficiency compared to TiO₂ in the degradation of several organic contaminants, which stimulated many researchers to further explore ZnO in many photocatalytic reactions [11–13]. The biggest advantage of ZnO compared with TiO₂ is that it absorbs over a larger fraction of the UV–vis spectrum than TiO₂ [14,15].

Suppression of the recombination of photogenerated electron–hole pairs in the semiconductors is essential for improving the efficiency of photocatalyst [16]. Doping is a very useful way to improve the charge separation in semiconductor systems and dopants such as Ag, Pt and Fe enhance the charge separation and reduce the electron–hole recombination [17–20]. Additionally, co-doping was also used to improve the photoactivity and there were a few reports on the synergistic effects of the co-doped TiO₂ or ZnO photocatalyst [21–24]. In addition, rare earth oxides are found to have good thermal stability due to their 4f electron and multi-electron configuration. Many studies had shown that Ce doping enhanced the photocatalytic activity of TiO₂ [25,26]. Lanthanide (Ln), Samarium (Sm) and Cerium (Ce)-doped TiO₂ nanoparticles (NPs) have been especially favored by their unique 4f electron configuration. Among others, Ce-doped TiO₂ nanoparticles have attracted much interest due to the Ce³⁺/Ce⁴⁺ redox couple. Therefore the present work is focused on the synthesis, characterization of the novel, reusable Ce–Ag–ZnO photocatalyst and its photocatalytic activity in the degradation of RR 120 dye under solar light.

2. Experimental

2.1. Materials

The commercial azo dye Reactive Red 120 (Fig. 1) from Balaji Colour Company, Dyes and Auxiliaries (Chennai) was used as received. Oxalic acid dihydrate (99%) and zinc nitrate hexahydrate (99%) were obtained from Himedia chemicals. AgNO₃ and Ce(NH₄)₄(SO₄)₄·2H₂O were obtained from spectrochem. ZnO (Himedia), TiO₂ (Merck) were used as received. A gift sample of Degussa TiO₂-P25 was obtained from Evonik (Germany). It is a 80:20 mixture of anatase and rutile. It has a particle size of 30 nm and BET surface area 50 m² g⁻¹. K₂Cr₂O₇ (s.d.fine), Ag₂SO₄ (s.d.fine), HgSO₄, FeSO₄·7H₂O (Qualigens) and H₂O₂ (Rankem) were used as received. The double distilled water was used to prepare experimental solutions. The pH of the solutions before irradiation was adjusted using H₂SO₄ or NaOH.

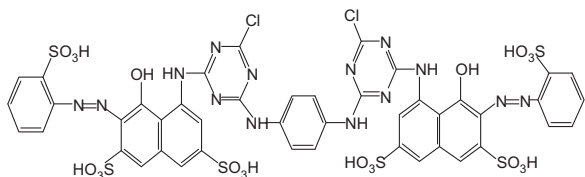


Fig. 1. Chemical structure of RR 120.

2.2. Analytical methods

Powder X-ray diffraction patterns were obtained using X'Per PRO diffractometer equipped with a CuK α radiation (wavelength 1.5406 Å) at 2.2 kW Max. Peak positions were compared with the standard files to identify the crystalline phase. For transmission electron microscope (TEM) images, the grids were dried under natural conditions and examined using a TEM Hitachi H-7500. The morphology of catalyst was examined using a JEOL JSM-6701F cold field emission scanning electron microscope (FE-SEM). Before FE-SEM measurements, the samples were mounted on a gold platform placed in the scanning electron microscope for subsequent analysis at various magnifications. Diffuse reflectance spectra were recorded using Shimadzu UV-2450. Photoluminescence (PL) spectra at room temperature were recorded using a Perkin Elmer LS 55 fluorescence spectrometer. The nanoparticles were dispersed in carbon tetrachloride and excited using light of wavelength 300 nm. Cyclic voltammetry (CV) measurements were carried out using CHI 60AC electrochemical analyzer (CHI Instruments Inc. USA). X-Ray photoelectron spectra of the catalysts were recorded in an ESCA-3 Mark II spectrometer (VG scientific Ltd., England) using AlK α (1486.6 eV) radiation as the source. The spectra were referenced to the binding energy of C1s (285 eV). The specific surface areas of the samples were determined through nitrogen adsorption at 77 K on the basis of BET equation using a Micromeritics ASAP 2020 V3.00H. UV spectral measurements were done using Hitachi-U-2001 spectrometer.

2.3. Irradiation experiments

All photocatalytic experiments were carried out under similar conditions on sunny days between 11 am and 2 pm. An open borosilicate glass tube of 50 mL capacity, 40 cm height and 20 mm diameter was used as the reaction vessel. The suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between dye and Ce–Ag–ZnO. Fifty milliliters of dye solution with Ce–Ag–ZnO was continuously aerated by a pump to provide oxygen and for the complete mixing of reaction solution. During the illumination time no volatility of the solvent was observed. After dark adsorption the first sample was taken. At specific time intervals 2–3 mL of the sample was withdrawn and centrifuged to separate the catalyst. One mL of the centrifugate was suitably diluted and its absorbance at 285 nm was measured. The absorbance at 285 nm represents the aromatic content of RR 120 and its decrease indicates the degradation of dye. For the degradation of 4-nitrophenol by UV-A light (365 nm, $I_{UV}=1.381 \times 10^{-6} \text{ E L}^{-1} \text{ s}^{-1}$), a Heber Multilamp-photoreactor HML MP 88 was used (Fig. 2). The intensity of solar light was measured using LT Lutron LX-10/A Digital Lux meter and the intensity was $1250 \times 100 \pm 100 \text{ lx}$. The intensity was nearly constant during the experiments.

3. Results and discussion

3.1. Characterization of catalyst

Preparation, characterization of 3 wt% Ce–Ag–ZnO and its photocatalytic activity for the degradation of AB 1 by

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