



Photocatalytic degradation of trypan blue and methyl orange azo dyes by cerium loaded CuO nanoparticles



R. Sasikala, K. Karthikeyan, D. Easwaramoorthy, I. Mohammed Bilal, S. Kutti Rani*

Department of Chemistry, B. S. Abdur Rahman University, Vandalur, Chennai, 600 048, India

ARTICLE INFO

Article history:

Received 2 March 2016

Received in revised form 9 June 2016

Accepted 11 July 2016

Keywords:

Ce loaded CuO

Photocatalysis

UV light

Trypan blue

Methyl orange

ABSTRACT

Pure and cerium loaded CuO nanoparticles (CCO NPs) were synthesized by a simple precipitation – thermal decomposition method and characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive spectra (EDS), diffuse reflectance spectra (DRS), photoluminescence (PL), X-ray photoelectron spectroscopy (XPS) and BET surface area measurements. The photocatalytic activity of pure, commercial and optimized Ce-loaded CuO catalyst was studied for the degradation of azo dyes such as Methyl Orange (MO) and Trypan Blue (TB) under UV light irradiation. CCO was found to be more competent in the degradation of two azo dyes than pure and commercial CuO. The mineralization of MO and TB has been confirmed by chemical oxygen demand (COD) measurements. A possible mechanism for the degradation was proposed for CCO. This catalyst can be reused and it was more stable without loss of their activity even at third cycles.

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1. Introduction

As an advanced oxidation process, heterogeneous photocatalysis was proficient in decaying waste water containing organic pollutants (Lam et al., 2012; Krishnakumar and Swaminathan, 2011), such as dyes (Muruganandham et al., 2006), effluent treatment (Yamauchi, 2013) and pharmaceutical compounds (Oveisi et al., 2012). Heterogeneous photocatalysis could be a potential technique for the degradation of these organic compounds since it allows mineralization of organic molecules to CO₂ and H₂O, and it avoids the secondary pollution. In this process, the property of photocatalytic material plays an important role, and thus, numerous photocatalysts have been developed to achieve the goal (Kimura et al., 2011). Moreover, the structural and morphological features of these photoactive materials have been demonstrated to be crucial in the degradation of modern pollutants (Subash et al., 2012; Subash et al., 2013; Georgekutty et al., 2008). Generally, the semiconducting materials such as TiO₂, NiO, ZnO, CuO, SnO₂, CdS, and ZnS perform as the best photosensitizers due to the electronic structure of the metal atoms in chemical composition, which is characterized by a filled valence band (VB) and an empty conduction band (CB) (Hoffmann et al., 1995).

Upon irradiation, the electrons in the valence band can be excited and jump up into the conduction band. These materials absorbed light energy as photon with energy equal or greater than its band-gap and thereby charge carriers are engendered. In order to have a photocatalyzed reaction, the e⁻h⁺ pair recombination, successive to the preliminary charge separation, must be prohibited as much as possible (Subash et al., 2013; Hoffmann et al., 1995). Among different semiconducting metal oxides, the commonly used semiconductor catalysts in photo induced processes are TiO₂, ZnO, CuO and NiO₂. Though these semiconductors have the drawback of not being activated by UV or visible light, it is highly profitable over the others as it is chemically and biologically static, photocatalytically stable and competent, fairly easy to synthesize, cheap and without risks to the environment (Subash et al., 2012; Subash et al., 2013). Especially, copper oxide (CuO), a well known p-type semiconductor with a slender bandgap of 1.2 eV in bulk, has been studied intensely (Basu Sinha et al., 2010; Mukherjee et al., 2011). Because of its versatile properties and potential applications, CuO is broadly used in heterogeneous photocatalysis (Gao et al., 2004), gas sensors (Poizot et al., 2000), lithium ion electrode materials (Venkatachalam et al., 2009), field-emission sources (Zhu et al., 2005) and semiconductors (Chen et al., 2003). However, pure CuO is not efficiently adequate for most of the photocatalytic reactions due to the fast recombination of the photo-generated e⁻-h⁺ pairs formed in a photocatalytic process.

One of efficient methods to alter the semiconductor surface is by using metals such as La, Er, Ag, Ce, Au, Mg etc., (Subash et al., 2013;

* Corresponding author.

E-mail addresses: skrani@bsauniv.ac.in, sasiaru16@gmail.com (S.K. Rani).

Georgekutty et al., 2008; Yang et al., 2014; Jinfeng et al., 2012; Wu et al., 2006; Etacheri et al., 2012). When these metals are loaded with CuO, charge transfer takes place from the CuO surface to the metal, suppressing the recombination of charge carriers, in consequence leading to enhanced photo catalytic activity. The purpose of the present work is mainly focused on the preparation, characterization and photo catalytic activity of cerium loaded CuO NPs, and also the degradation studies of Tryphan Blue (TB) and Methyl Orange (MO) under UV light irradiation. The mineralization of both dye molecules was also confirmed by chemical oxygen demand (COD) measurement.

2. Experimental

2.1. Materials

The commercial azo dyes, TB, MB were from SD Fine (Fig.S1), Oxalic acid dihydrate (99%) and copper nitrate pentahydrate (99%) were obtained from Himedia chemicals. $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ (CAS) was obtained from Spectrochem, commercial CuO (Himedia), $\text{K}_2\text{Cr}_2\text{O}_7$ (S.D. fine), Ag_2SO_4 (S.D. fine), HgSO_4 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Qualigens) were used as received. The appropriate solutions were prepared in double distilled water. Before irradiation the pH of the solutions was adjusted using H_2SO_4 or NaOH.

2.2. Preparation of Ce loaded CuO NPs

Ce loaded CuO was synthesized by simple precipitation- thermal decomposition method. Aqueous solutions of 100 mL of 0.4 M copper nitrate pentahydrate and 100 mL of 0.6 M oxalic acid in deionized water were brought to their boiling points separately. When the oxalic acid solution was added to the solution of copper nitrate, copper oxalate was formed. Then, 5 mL of 0.122 g of $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ (CAS) solution was added with the solution of copper oxalate suspension and this mixture was stirred for 1 h at 70 °C. Then the mixture was cooled to room temperature, the Ce containing copper oxalate was washed several times with distilled water, air-dried overnight and dried at 100 °C for 5 h. Calcination of the mixed precipitate at 450 °C for 5 h resulted in the formation of CCO NPs. This catalyst contained 1 wt% of Ce. Using the same procedure 0.5, 1.5, and 2.0 wt% of Ce loaded CuO were prepared. The bare CuO without addition of CAS was prepared by the same procedure with respective precursors. In order to know the decomposition temperature of copper oxalate, TG-DTA measurements were made for catalyst before calcination and their results are shown in Fig. S2 (see Supporting information). The thermal properties of as-prepared copper oxalate were investigated by thermogravimetric analysis (TG) and differential thermal analysis (DTA) in nitrogen atmosphere as shown in Fig. S2. The small weight loss before 230 °C can be attributed to the emission of H_2O in the form of physical and chemical absorption. A large, sharp weight loss in the temperature range of 250–315 °C in the TG curve (Fig. S2(a1)), and a strong exothermic peak at 310 °C in the DTA curve (Fig. S2(a2)) were observed, and were mainly attributed to the decomposition of copper oxalates (Bharat Kumar et al., 2013). No considerable weight loss could be observed above 350 °C, suggesting the formation of crystalline CuO as a decomposition product.

The thermal properties of as-prepared cerium containing copper oxalate were investigated by thermogravimetric analysis (TG) and differential thermal analysis (DTA), as shown in Fig. S2(b). The small weight loss before 240 °C can be attributed to the dehydration of H_2O molecules present in oxalates. A large, sharp weight loss was observed in the temperature range of 240–340 °C in the TG curve (Fig. S2(b1)), and a sharp exothermic peak at 340.6 °C (Fig. S2(b2)) with the formation of stable cerium oxide from the decomposition

of copper oxalates (Vimal et al., 2015). After 350 °C, no considerable weight loss could be observed which indicates the stability of the product.

2.3. Analytical methods

Powder X-ray diffraction patterns were obtained by using an X'Per PRO diffractometer equipped with a $\text{CuK}\alpha$ radiation (wavelength 1.5406 Å) at 2.2 kW Max. Peak positions were compared with the standard files to identify the crystalline phase. The morphology of the catalyst was examined using a JEOL JSM-6701F cold field emission scanning electron microscope (FE-SEM) equipped with OXFORD energy dispersive X-ray spectrum (EDS). 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 was recorded using Shimadzu UV-2450. Photoluminescence (PL) spectra was recorded at room temperature using a Perkin Elmer LS 55 fluorescence spectrometer. The nanoparticles were dispersed in carbon tetrachloride and excited at a wavelength of 300 nm. 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 V3.00 H surface area analyser. UV irradiation studies were done using Hitachi-U-2001 spectrometer. Chemical oxygen demand (COD) measurements were carried out by a reported procedure (Krishnakumar and Swaminathan, 2011).

2.4. Photocatalytic experiments

A Heber Multilamp-photoreactor HML MP 88 was employed Fig. S3 (Muthu et al., 2009) for the degradation by UV-A light (365 nm). This reactor consists of 8 W medium pressure Hg vapour lamps set in similar wavelength emitting 365 nm. It has a reaction chamber with specially designed reflector made of polished aluminum and built in cooling fan. It is fixed with a magnetic stirrer and 50 mL capacity reaction glass tubes. The light coverage length is 330 mm. The irradiation was carried out by means of four parallel 8 W medium pressure Hg lamps. The solution with photo catalyst as well as dye solution was persistently aerated by a pump to supply oxygen and for absolute mixing of reaction solution and catalyst.

25 mL of dye solution (TB and MO) with the suitable concentration as well as the amount of catalyst was stirred for 30 min in the absence of light prior to illumination in order to achieve maximum adsorption of dye onto the surface of the catalyst. Throughout the illumination time no volatility of the solvent was observed. At specific time intervals, 2–3 mL of sample was withdrawn and catalyst was removed by centrifugation. The changes in the concentration of two different dyes were observed from their characteristic absorption at UV and visible region using UV-vis spectrophotometer. The absorbance at 200–400 nm corresponds to the aromatic part of the dyes and the disappearance of absorbance indicates the degradation of dye molecule.

2.5. Chemical oxygen demand (COD) measurements

COD measurements are used to verify the complete mineralization process using the subsequent procedure. For two hours, the sample was refluxed with HgSO_4 , known volume of standard $\text{K}_2\text{Cr}_2\text{O}_7$, Ag_2SO_4 and H_2SO_4 . Then, using ferroin as indicator, the sample was titrated with standard ferrous ammonium sulfate (FAS). COD was determined using the following Eq. (1)

$$\text{COD} = \frac{(\text{Blank titer value} - \text{dye sample titre value}) \times \text{normality of FAS} \times 8 \times 1000}{\text{Volume of sample}} \quad (1)$$

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