Ecotoxicology and Environmental Safety 134 (2016) 412–420

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Enhanced visible photocatalytic activity of cotton ball like nano structured Cu doped ZnO for the degradation of organic pollutant

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ARTICLE INFO

Article history:
Received 6 December 2014
Received in revised form
1 October 2015
Accepted 26 October 2015
Available online 11 November 2015

Keywords:
Photocatalyst
Visible light
Degradation
Tri-azo dye
Reusability

ABSTRACT

Stringent Environmental standards followed worldwide led to the emergence of advanced oxidation process for the removal of toxic contaminants from water and wastewater. Among all semiconductor photocatalysts have great potential in the degradation of organic and inorganic pollutants into lesser harmful products under visible light irradiations. The present research work describes the synthesis of Cu doped ZnO (CuDZ) via a co-precipitation method to attain high crystallized powder confirmed by XRD analysis. The FE-SEM images showed that the CuDZ has cotton ball like morphology with a uniform size ranged from 25 to 40 nm. TEM, FT-IR and UV-DRS studies of the synthesized CuDZ are also discussed in detail. The photocatalytic activity of the as prepared CuDZ catalyst was tested for the degradation of Direct Blue 71 (DB 71) dye in aqueous phase under visible light irradiation. The degree of degradation was found to be dependent on aqueous phase pH, duration of irradiation time, amount of photocatalyst, the initial dye concentration and kinetics of photodegradation. The maximum photocatytic degradation of DB 71 dye was found to be effective at pH 6.8. The optimum amount of photocatalyst was found $3\ g\ L^{-1}$ of CuDZ for the complete degradation of DB 71 dye ($0.01\ g\ L^{-1}$). The reusability of the photocatalyst indicates that 96% of DB 71 dye was degraded up to 3rd cycles of use. The visible photodegradation of DB 71 dye was exhibited pseudo-first-order kinetics. Chemical oxygen demand and ESI-MS studies confirmed the complete mineralization of DB 71 dye molecules.

1. Introduction

The residues of textile and other coloring industries are the major pollutants to contaminate water and affect the aquatic life as well as human life (Mekasuwandumrong et al., 2010). The colored organic dyes from industries are mostly non-biodegradable in nature, creating major problems to the aquatic creatures and severely disturb the water ecosystem (Ameen et al., 2012). In general, the remediation of organic dyes is performed by the conventional treatment like chemical precipitation/separation, coagulation, ozone oxidation, hypochlorite oxidation, electrochemical method and adsorption (Daneshvar et al., 2007). The photocatalytic degradation is an efficient and easy method for the decomposition of harmful organic pollutants into less hazardous minerals (Ameen et al., 2010; Kuriakose et al., 2014; Ahmad et al., 2013; Wu et al., 2012). Recently, the semiconductor materials have been applied as capable photocatalyst for the effective degradation of contaminants for purifying water (Jia et al., 2012).

Zinc Oxide (ZnO) have wide direct band-gap energy (3.37 eV) and a large exciton binding energy (60 meV), is an attractive semiconductor due to its low toxicity, high stability and high transparency in the visible wavelength. This makes it worthy in the potential and established hi-tech applications such as surface acoustic wave devices (Carlotti et al., 1987), blue and ultraviolet light emitters (Bagall et al., 1997), transparent electrode (Srikant et al., 1995), solar cell windows (Jeong et al., 2006), photovoltanic devices (Pauporte and Lincot, 2000), gas sensors (Devi et al., 2006), photocatalysis (Song and Zhang, 2012), etc. It is known that ZnO material can be made with the most diverse and abundant configurations of nanostructures such as quantum dots, rods, wires, belts, springs, bows, helices and prisms. For photocatalysis, ZnO has also been considered as a suitable alternative for TiO_2 due to its similar band-gap and lower cost (Hariharan, 2006). Moreover, it exhibits better performance in the degradation of organic dye molecule in both acidic and basic media. The intrinsic defects of ZnO are beneficial for setting up catalytic systems, which are expected to degrade the environmental contaminants. The photocatalytic activity of nano structured ZnO is expected to be enhanced not only because of their increased surface area but also because of changes of surface properties such as surface defects

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Abbreviations: ZnO, Zinc oxide; TiO_2, Titanium dioxide; CuDZ, Cu doped ZnO; DB 71, Direct Blue 71; COD, Chemical Oxygen Demand; μm, micrometer; ml, Milliliter; min, minutes; h, hour; mm, millimeter; nm, nanometer; cm, centimeter; g, gram

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http://dx.doi.org/10.1016/j.ecoenv.2015.10.030
0147-6513/

(Rezapour and Talebian, 2011). It has been widely proved that modifications of oxide semiconductors, including doping of transition metals or rare earths, could enhance their properties (Subash et al., 2012, 2013; Krishnakumar and Imae 2014; Krishnakumar et al., 2014). The photocatalytic properties of ZnO were greatly enhanced when modified with the incorporation of dopant ions (Donkova et al., 2010). The doping of metal ions in ZnO nanostructures can lead to effects such as enhancement/decrease in fluorescence and controlling concentration of surface defects. The doping of Cu in ZnO is expected to modify absorption, and other physical or chemical properties of ZnO because of the different structure of the electronic shell and the similar size of Cu and Zn. Cu can enter the ZnO lattice substitutionally as deep acceptors in combination with a neighboring O vacancy (Kanai, 1991). Hence, in the present work cotton ball like nano structured CuDZ were synthesized with different doping concentrations through the co-precipitation method and their photocatalytic activities were evaluated for the degradation of DB 71 dye.

2. Experimental methods

2.1. Materials

DB 71 dye (C.I. No.: 4399-55-7; molecular weight=965.94), Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and copper acetate tetrahydrate ($Cu(CH_3COO)_2 \cdot 4H_2O$) was procured from S.D. Fine Chemicals Ltd., Mumbai, India. Sodium hydroxide (Na_2CO_3) was obtained from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. Hydrochloric acid (HCl) was procured from Ranbaxy Fine Chemicals Ltd., New Delhi, India. All the chemicals were of analytical reagent grade quality and were used as received. Dye solutions were prepared by dissolving appropriate amount of the dye in double distilled water before each experiment.

2.2. Analytical methods

The characteristics of the final product was characterized by X-ray powder diffraction (XRD) analysis employing X' per PRO, Perkin Elmer 6X FT-IR spectrophotometer was used for recording FT-IR spectra, Transmission electron microscope (TEM) images were recorded using a Philips model (Tecnai 10) transmission electron microscope and the morphology of catalyst was examined using a HITACHI-SU6600 field emission scanning electron microscope (FE-SEM). UV–vis-Diffuse reflectance spectra were recorded using shimadzu UV-2450. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an K-Alpha™+ spectrometer. Thermogravimetric analysis was carried out in TGA-Thermal Analyst NETZSCH STA 409 PC at a heating rate of 10 °C/min from room temperature to 800 °C. The elution profiles were monitored at 254 nm and ESI-Mass spectrometer-LCQ Advantage MAX, Thermo Finnigan.

2.3. Preparation of CuDZ catalyst

CuDZ catalyst was prepared according to the modified literature (Tsuzuki et al., 2009). Typical procedure was as follows: 13.5 g of zinc acetate dihydrate, 6.5 g of sodium carbonate and 1.3987 g (0.25%), 2.7975 g (0.5%), 4.1961 g (0.75%), 5.595 g (1%) and 8.3925 g (1.5%) of copper acetate tetrahydrate ($Cu(CH_3COO)_2 \cdot 4H_2O$) were separately dissolved in 50 ml of deionised water. Mixed with zinc acetate dihydrate and copper acetate tetrahydrate solutions with uniform dispersions and then Na_2CO_3 solution was added drop wise under constant stirring to form metal (Cu, Zn) carbonates as a white precipitate. The precipitates were separated from the supernatant by filtration and washed with deionised water until the salinity becomes less than 0.1 g/L. The separated precipitates were dried in hot air oven at 60 °C and then sintered at 300 °C in a muffle furnace for 1 h. Finally CuDZ catalyst was obtained.

2.4. Photocatalytic experiments

The visible light photocatalytic experiments were conducted in a visible light slurry photoreactor supplied by Heber Scientific Company, Chennai, India. The schematic diagram of the visible light slurry photoreactor already been reported elesewhere (Thennarasu and Sivasamy, 2013). Briefly, the slurry photoreactor is equipped with a magnetic stirrer, 500 W tungsten lamp (wavelength=400–780 nm and Intensity=~10,000 lx) attached with water circulating glass reactor, highly polished anodized aluminum reflector and cooling fans were housed at the bottom of the reactor to dissipate the generated heat during the photocatalytic experiments. Borosilicate glass tube of ~15 mm inner diameter was used as the reaction vessel and it was placed at the center. The distance between the light source and the reaction vessel was ~15 cm. The photocatalytic activity of CuDZ catalyst towards DB 71 dye was performed. In brief, 0.3 g of as synthesized CuDZ catalyst was added in 100 mL solution of DB 71 dye (0.01 g/L) under continuous stirring. The suspension was continuously stirred for 30 min to obtain the adsorption–desorption equilibrium between DB 71 dye and CuDZ photocatalyst under dark condition. Finally, the visible light illumination was used to stable the aqueous dye suspension under constant stirring. The decomposed dye was taken out (5 mL) with regular interval (for kinetics – 0, 5, 10, 15, 20, 25, 30, 45, 60, 90, 120, 150, 180, 240 min) and subjected to filtration (using whatman, pore size=11 µm, thichnes=180 µm) to separate out the photocatalyst. By UV–visible spectrophotometer, the absorption spectrum of decomposed dye was recorded. The degradation rate of DB 71 dye over CuDZ catalyst is estimated by the following equation (Eq. (1)):

$$\text{Degradation rate } (\%) = \left(C_0 - C/C_0\right) \times 100 \tag{1}$$

where C_0 is the initial DB 71 dye concentration, C is the concentration of DB 71 dye after visible irradiation. The duplicate photocatalytic experiments were conducted simulatanesouly and errors were found within 5% for all the paramters.

3. Results and discussion

XRD patterns of copper doped (with different concentrations such as 0.25, 0.5, 0.75,1.0 and 1.5%) onto ZnO catalyst are shown in Fig. 1(i). Scherrer equation $d=0.94\lambda/\beta\cos\theta$ was used to calculate the average crystallite size and it was in the range of 5–29, 5–14, 15–110, 6–11 and 32–72 nm for 0.25, 0.5, 0.75, 1, 1.5% of CuDZ catalyst respectively. λ denotes the wavelength of the radiation equal to 0.154 nm, β is the full width at half maximum (FWHM) and θ is the half diffraction angle. It was observed that peaks corresponding to the ZnO wurtzite phase were mainly found in the XRD patterns of CuDZ catalyst. The standard diffraction peaks shows that the crystal structure of ZnO catalyst is a hexagonal wurtzite structure (JCPDS data card No. 36-1451) with preferred orientation along (101) plane in all the samples. This is the most stable phase of ZnO. It was observed that with increasing the dopant concentration (from 0.25 to 1.5%) the intensity of the ZnO peaks increased which was caused by the increases in the crystallinity of ZnO. XRD measurements showed that there is an additional peak (2θ=32.38, 38.08, 53.45, 59.24 and 27.72) which corresponding to the plan (110, 111, 020, 202 and 110) for 0.25% catalyst, which is due to the impurity phases such as CuO (JCPDS