Journal of Hazardous Materials 172 (2009) 700–706

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Effect of temperature on the formation of macroporous ZnO bundles and its application in photocatalysis

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ARTICLE INFO

Article history:
Received 16 April 2009
Received in revised form 13 July 2009
Accepted 14 July 2009
Available online 22 July 2009

Keywords:
ZnO
Bundles
Photocatalyst
Methylene blue

ABSTRACT

In this article, the effects of temperature on the formation of macroporous zinc oxide bundles and its photocatalytic activity under a variety of experimental conditions were reported. Thermal decomposition of zinc oxalate dihydrate yields hexagonal wurtzite-type ZnO bundles. Increased the decomposition temperatures resulted in decreased time required for bundle formation, with a corresponding increase in nanoparticles agglomeration. ZnO bundle formation was facilitated up to 200 °C after complete decomposition of zinc oxalate into ZnO at 400 °C in 15 min. However, low temperature (such as 100 °C) was not facilitated nanobundle formation, suggesting the importance of temperature on ZnO bundles formation. In addition, nitrogen adsorption experiments confirmed the presence of macroporous structure in the bundles. The photocatalytic decolorization and adsorption of methylene blue dye (MB) on ZnO bundles were investigated under UV light irradiation. The adsorption and decolorization efficiency of macroporous bundles were higher than the fused bundles. In conclusion, ZnO bundles are efficient and easily recyclable photocatalyst.

1. Introduction

Zinc oxide is a well-known wurtzite type wide-band gap semiconductor and currently gained attention because of its electronic properties. Recently, the study of one-dimensional (1D) nanostructural ZnO has attracted much interest owing to its low cost, unique electrical, optoelectronic and luminescent properties with many potential applications [1–5]. The synthesis and application of new ZnO nanostructures is on the cutting edge of today's research in nanotechnology. Such attempts in nanomaterial growth must be improved from naturally occurring processes in order to be scalable for their practical applications.

Photocatalytic processes in polluted air and water can degrade the concentration of contaminants through the use of UV-irradiated inorganic oxides. In recent years, novel heterogeneous metal oxide semiconductor materials, for example, TiO_2 and ZnO, were developed, which attracted considerable attention due to their photocatalytic ability to degrade various environmental pollutants [6–10]. ZnO is a most effective process, like TiO_2, in photocatalytic decolorization under UV irradiation. Certain studies have confirmed that ZnO exhibits a better efficiency than TiO_2 in photocatalytic decolorization of select dyes even in aqueous solutions [11–13]. Other advantages of ZnO application were reported an absorption capacity with larger fractions of solar spectrum compared to TiO_2 [14].

Synthetic dyes are major industrial pollutants as a water contaminant [15]. Textile wastewater frequently introduces intensive color and toxicity residues into aquatic systems. Due to the complex aromatic structures and stability of these dyes, conventional biological treatment methods are at times ineffective as a pollutant degrader [16,17]. In many applications, ZnO was used to form fine powder particulates suspended in water. In spite of the simplicity of this technique, it is still necessary to recover the ZnO powders after photocatalytic water treatment. Researchers have used other methods to immobilize ZnO powders on a supporting material while searching for a new, easily recoverable photocatalyst process to offset the cost of recovery operations, and possible powder loss [18,19]. Earlier, we reported the fabrication of easily recyclable, wurtzite ZnO bundles and their catalytic activity in catalytic ozonation processes using 2-ethoxy ethyl acetate (2-EEA) as a model pollutant [1].

ZnO bundle synthesis under optimum experimental condition is necessary for large scale production and for energy saving purposes. Since we previously reported that the decomposition temperature played a crucial role in the formation of bundles, the practical effects of temperature on bundles formation needed further investigation. Although zinc oxalate was used as a starting material for the preparation of ZnO, no research results were available for ZnO bundle fabrication [20–22]. The aim of the present investigation was to study the ZnO bundle formation under a variety of experimental conditions, including adsorption and photocatalytic efficiency rates

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doi:10.1016/j.jhazmat.2009.07.053

using MB as a model pollutant under UV light irradiation. MB dye is not regarded as an acutely toxic component, but it has various harmful effects. Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice and quadriplegia and tissue necrosis in humans. Although MB is frequently seen in some medical uses in large quantities, it can also be widely used in coloring paper, dyeing cottons, wools, coating for paper stocks, etc.

2. Materials and methods

2.1. Chemicals

Methylene blue dye was obtained from Merck chemical company, Germany. Oxalic acid (anhydrous) (99%) and zinc nitrate hexa hydrate (99%) were purchased from SHOWA Chemical Co., Japan.

2.2. Preparation of zinc oxalate dihydrate

Aqueous solutions of equal volume of 0.4 M zinc nitrate hexa hydrate and of 0.6 M anhydrous oxalic acid in deionized water (Milli q-Plus, resistance = 18.2 MΩ) were brought to their boiling points and the former was added rapidly to the latter; the mixture was stirred often as it cooled down to room temperature. The precipitate is rather fine and uniform in dimension. The crystals were washed several times with distilled water, air-dried for over night, and dried 100 °C for 3 h. The sample was kept for further analysis in polyethylene cover.

2.3. Synthesis of ZnO bundles

About 1 g of zinc oxalate dihydrate was taken in a porcelain dish and kept inside the muffle furnace. The furnace was heated at the rate of 20 °C/min to reach the desired decomposition temperature. After desired time, the furnace was allowed to cool down automatically to room temperature. The synthesized ZnO bundle was collected and used for further analysis.

2.4. Photocatalytic reactor

The photocatalytic decomposition experiments were studied in an immersion type photoreactor which was assembled in our laboratory as shown in Fig. 1. This module consists of a double-walled glass vessel with its outer circulation space connected to a water bath for maintaining desired temperatures. Open borosilicate glass tubes of 200 ml capacity, with a 30 cm height and a 6 cm diameter, were used as reaction vessels. Required quantities of dye solution with catalyst were placed in the inner reactor as a decomposition experiment. In the center of cylindrical reactor, a lamp was placed inside the quartz tube (19 cm height, 2 cm diameter) in open-air conditions. A low-pressure mercury lamp (Pen-Ray, UVP Inc.) was used for irradiation purpose, which predominantly emits sole wavelength at 254 nm and has an intensity of 5.5 mW/cm^2 measured by UVX radiometer, UVP Inc. The temperature of the experimental solution was maintained at 25 °C by circulating water during the experiments. The aforementioned apparatus was placed in a magnetic stirrer for complete mixing of the catalyst with dye solution. In all cases, 50 ml of the MB dye solution (100 mg/l) containing appropriate quantity of the ZnO was used. The suspension was stirred for 30 min in the dark for the attainment of adsorption equilibrium. At specific time intervals, 4 ml of the sample was withdrawn and centrifuged to separate the catalyst. One milliliter of the centrifugate was diluted to 25 ml and its absorbance at 665 nm was measured. The maximum absorbance intensity at the wavelength of 665 nm was experimentally determined using a spectrophotometer (Spectronics, Genesys 5, USA) and it is used to monitor the decolorization of methylene blue (C.I. number 52015, molecular formula = $C_{16}H_{18}N_3ClS{\cdot}H_2O$, molecular weight = 355.89). The calibration curve obtained using solutions of known concentrations of the studied MB and was linear with a high correlation coefficient (R^2) 0.999. From this calibration curve, the initial and final concentration of MB was calculated as necessary.

2.5. Adsorption of MB on ZnO bundles

All adsorption experiments were carried out using a 5 mg/l of MB with 1 g/l of catalyst prepared at a neutral pH 6.9. Approximately 25 ml of dye solution with catalyst was collected in a polyethylene bottle and kept in a thermo-stated mechanical shaker for 24 h at 25 °C. After adsorption process, the catalyst was filtered and centrifuged from interfering concentration measurement. In order to avoid any photoreaction of ZnO on MB, the samples were kept in the dark for the entire period of the experiment.

2.6. Analytical methods

The X-ray diffraction (XRD) patterns were recorded using a MAX SCIENCE MXP3 diffractometer and Cu Kα radiation and 2θ scanned angle from 25° to 80° at the scanning rate of 2° per min. The surface area, pore size and pore volume of the ZnO bundles were mea-

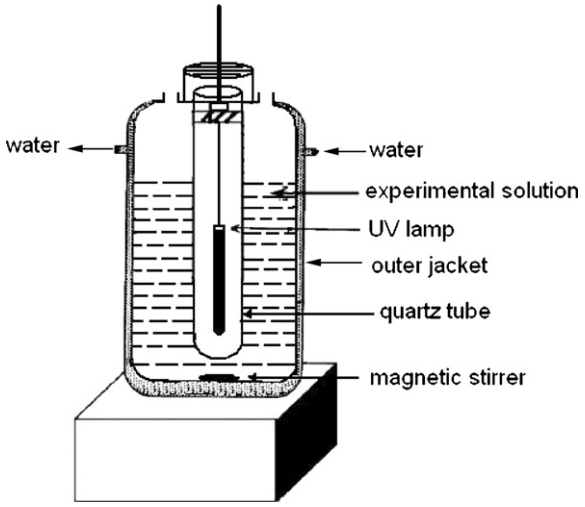

Fig. 1. Schematic diagram of photocatalytic reactor under UV light irradiation.

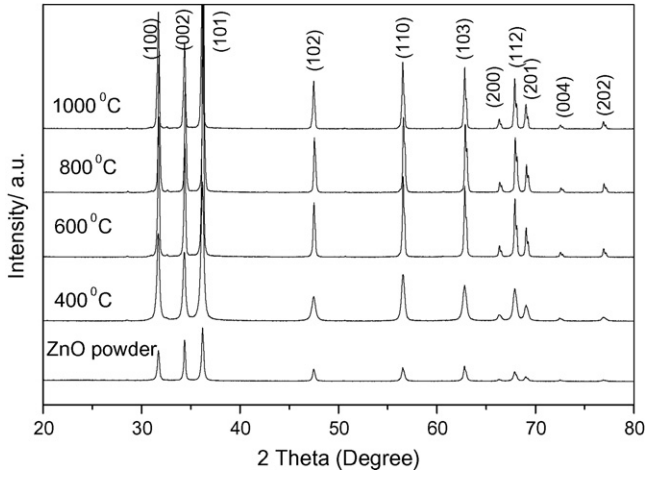

Fig. 2. XRD of ZnO powder and bundles formed at various decomposition temperatures.