



Rapid microwave hydrothermal synthesis of ZnGa_2O_4 with high photocatalytic activity toward aromatic compounds in air and dyes in liquid water

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ABSTRACT

ZnGa_2O_4 was synthesized from $\text{Ga}(\text{NO}_3)_3$ and ZnCl_2 via a rapid and facile microwave-assisted hydrothermal method. The photocatalytic properties of the as-prepared ZnGa_2O_4 were evaluated by the degradation of pollutants in air and aqueous solution under ultraviolet (UV) light illumination. The results demonstrated that ZnGa_2O_4 had exhibited efficient photocatalytic activities higher than that of commercial P25 (Degussa Co.) in the degradation of benzene, toluene, and ethylbenzene, respectively. In the liquid phase degradation of dyes (methyl orange, Rhodamine B, and methylene blue), ZnGa_2O_4 has also exhibited remarkable activities higher than that of P25. After 32 min of UV light irradiation, the decomposition ratio of methyl orange (10 ppm, 150 mL) over ZnGa_2O_4 (0.06 g) was up to 99%. The TOC tests revealed that the mineralization ratio of MO (10 ppm, 150 mL) was 88.1% after 90 min of reaction. A possible mechanism of the photocatalysis over ZnGa_2O_4 was also proposed.

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1. Introduction

With the development of industry in the past decades, the living environment for human has been seriously polluted by the discharges from factories. For example, benzene and its homologue are widespread existed in polluted urban atmospheres. However, one recent report showed that benzene, even at a low level of 1 ppmv, can reduce blood cell counts and cause hematotoxicity in factory workers [1,2]. Benzene has already been regarded as the priority hazardous substance because of its high toxicity, confirmed carcinogenicity, and environmental persistence [3]. Thus, how to improve the living conditions for human by removing benzene and its homologue from the ambient environment has attracted great attention, and people have do great efforts in this aspect.

Photocatalysis, as a green technology, offers the potential method for complete elimination of toxic chemicals [4–7]. For example, the TiO_2 -based photocatalytic oxidation (PCO) has been recognized as a very promising technology for environmental remediation. However, some previous research work proved that TiO_2 was often rapidly deactivated in the treatment of aromatics

compounds in the gas phase, due mainly to accumulation of less-reactive byproducts on the photocatalyst surface [8–10]. Further research works have found that adding proper quantity of water vapor into the reaction system could slightly meliorate the catalyst's durability [10–12]. However, such a low inherent conversion is not significant for practical application. Recently, developing non- TiO_2 photocatalyst has become one hot topic, and some novel photocatalysts have been reported which could degrade benzene at ambient conditions.

ZnGa_2O_4 with spinel-type structure has received much attention due to its potential applications, such as a low voltage field emission display (FED), or a vacuum fluorescent display (VFD) [13–17]. The synthesis of ZnGa_2O_4 has been examined mostly by traditional solid-state reaction [13,16–20], combustion method [19], template method [20], soft-chemical method [21], and co-precipitation method [22]. Sol-gel and sputtering processes have also been tried for the preparation of ZnGa_2O_4 thin films [23–26]. However, most of these methods are time- and energy-consuming, or the synthetic process is too sophisticated to master. On the contrary, the microwave hydrothermal (M-H) method has attracted a lot of interest in the past many years. The advantages of this method are: (1) rapid heating to temperature of treatment; (2) increased reaction kinetics by one to two orders of magnitude; (3) formation of novel phases; (4) selective crystallization; and (5) low energy consumption and time saving [27–29]. Conrad et al. [30]

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have ever reported the M–H synthesis of ZnGa_2O_4 , but the specific surface area of the product was relatively small ($63 \text{ m}^2 \text{ g}^{-1}$), which was very bad for the improvement of photo-activity. Herein, we report the rapid M–H synthesis of ZnGa_2O_4 with large surface area and high photocatalytic activity toward organic pollutants in air and water. ZnGa_2O_4 was found to have shown superior photocatalytic activities toward environmental pollutants (e.g., benzene, toluene, MO, and RhB) under UV light irradiation. Our studies imply that microwave hydrothermal method is very promising for synthesizing novel photocatalysts.

2. Experimental section

2.1. Preparation of photocatalysts

All of the reagents are used without further purification. The nanocrystalline ZnGa_2O_4 photocatalyst was prepared via M–H method. The M–H synthesis was performed in a single mode CEM Discover System (Explorer48, CEM Co., and USA) operating at 200 W, 2.45 GHz. In a typical procedure, $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and ZnCl_2 were firstly dissolved into distilled water, the atomic ratio of Ga/Zn in the solution was 2:1. Under continuous stirring, ammonia solution was added into the mixed solutions. White precipitate was firstly produced and then dissolved because of the excessive addition of ammonia solution. The resulting transparent solution was then loaded into a 35 mL vessel (20–25 mL reaction volume), which was treated at 160°C for 20 min using the microwave system. After cooling to room temperature, the product was collected, washed with distilled water several times, and finally dried in air at 60°C overnight. All of the hydrothermal treatment was made in the absence of any dispersant or capping organic agent, avoiding the pollution of environment.

2.2. Characterization of photocatalysts

The phase constitution of the product was determined by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer at 40 kV and 40 mA with Ni-filtered Cu K_α radiation. The crystallite size was calculated from peak half-width by using Scherrer equation with corrections for instrumental line broadening. The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were measured by a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. Carbon-coated copper grid was used as the sample holder. The optical properties were analyzed by UV–Vis diffuse reflectance spectroscopy (DRS) using a UV–Vis spectrophotometer (Cary–500, Varian Co.) equipped with an integrating sphere attachment. Nitrogen sorption experiments were carried out at 77 K by using Micromeritics ASAP2020 equipment. X-ray photoelectron spectroscopy (XPS) analysis was conducted on an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific) at 3.0×10^{-10} mbar using Al K_α X-ray beam (1486.6 eV).

2.3. Tests of photocatalytic activity

The gas phase photocatalytic degradation of benzene was conducted in a tubular vessel microreactor operating in a continuous-flow mode. All catalysts were sieved to obtain particles of the 0.21–0.25 mm size. Four 4 W UV lamps with a wavelength centered at 254 nm (Philips, TUV 4 W/G4 T5) were used as the light source (light intensity: 4.8×10^{16} quants $\text{cm}^{-2} \text{ s}^{-1}$). A bubbler that contained benzene was immersed in an ice–water bath and benzene (about 220 ppmv) bubbled with oxygen from the bubbler was fed to 0.3 g of catalyst at a total flow-rate of 20 mL min^{-1} .

The temperature of the reactions was controlled at $39 \pm 1^\circ\text{C}$ by air-cooling system and circulating cold water. Analysis of the reactor effluent was conducted by a gas chromatograph (HP6890). The concentrations of benzene and carbon dioxide were determined by using the FID and TCD detectors, respectively. The adsorption–desorption equilibrium of benzene gas on sample was obtained after 10 h in dark before lights turn on. Benzene was found to be thermally stable in the reactor without illumination. The degradation of toluene and ethylbenzene was conducted under the same conditions except for the initial concentrations. As a comparison, the photocatalytic activity of commercial P25 (Degussa Co.) catalyst was also tested under the same conditions with an equal amount of catalyst loaded.

The photocatalytic degradations of dyes (RhB, MO, and MB) in liquid phase were conducted in a quartz tube with 4.6 cm inner diameter and 17 cm length. Four 4 W UV lamps with a wavelength centered at 254 nm (Philips, TUV 4 W/G4 T5) were used as illuminating source. A 0.06 g of photocatalyst was suspended in 150 mL of dye solution with a certain concentration and stirred for 1 h to ensure the establishment of adsorption–desorption equilibrium. A 3 mL of aliquot was taken at a certain time interval during the experiment and centrifuged (TDL-5-A) to remove the powders. The filtrates were analyzed on a Varian UV–Vis spectrophotometer (Cary–50, Varian Co.). The percentage of degradation is reported as C/C_0 . C is the absorption of pollutants at each irradiated time interval of the main peak of the absorption spectrum. And C_0 is the absorption of the initial concentration when adsorption–desorption equilibrium was achieved. As a comparison, 0.06 g of TiO_2 P25 (Degussa Co.) was used as a kind of standard, and its photocatalytic activity was tested under the same conditions. In the total organic carbon (TOC) investigation, the photocatalytic reaction was conducted under the same condition except that the reaction time was prolonged to 180 min.

3. Result and discussion

Fig. 1 shows the typical XRD patterns of ZnGa_2O_4 sample. As it can be seen, all the patterns can be identified as a single cubic phase of ZnGa_2O_4 (JCPDS no. 38-1240) with spinel structure, no trace of extra peaks has been detected. Seven distinctive peaks at 18.4° , 30.3° , 35.7° , 43.4° , 53.8° , 57.4° and 63.0° match well with the (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) crystal planes of ZnGa_2O_4 , respectively. The average crystallite sizes calculated from the Scherrer equation are about 13.8 nm.

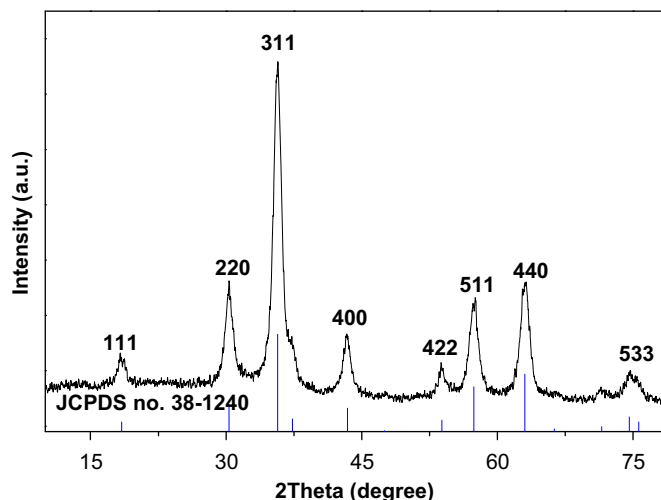


Fig. 1. XRD patterns of the as-prepared ZnGa_2O_4 sample.

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