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Photocatalytic activities of a novel $ZnWO_4$ catalyst prepared by a hydrothermal process

Hongbo Fu, Jie Lin, Liwu Zhang, Yongfa Zhu *

Department of Chemistry, Tsinghua University, Beijing 100084, PR China

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Abstract

$ZnWO_4$ catalysts have been successfully synthesized by a hydrothermal crystallization process. $ZnWO_4$ catalyst synthesized at 180 °C for 24 h exhibited relatively high photochemical activity for the decomposition of rhodamine-B, and showed better activity for the degradation of formaldehyde than that of TiO_2 (P-25). The generations of the photocurrent and H_2 evolution from pure water were also realized. UV bands observed in the catalyst were assigned to the band transition from the occupied O 2p orbitals to the empty W 5d orbitals. On the basis of the analysis of the energy levels and the band structures, the photocatalytic mechanism of the catalyst was also discussed.

Keywords: $ZnWO_4$; Photocatalyst; Nanorod; Rhodamine-B; Formaldehyde

1. Introduction

During the past decades, heterogeneous photocatalysis has been studied extensively from the viewpoint of environmental accountability and energy conversion [1–3]. TiO_2 has been dominantly used because of its high activity, long-term stability, low price, and availability. In the recent years, a growing interest was also focused on the non-TiO_2-based catalyzers [4–9]. Many mixed oxide photocatalysts such as Bi_2WO_6 [6,7], $NaTaO_3$ [8], and $CaIn_2O_4$ [9] have been reported to show high activity for the photodegradation of organic pollutants or/and water decomposition. $ZnWO_4$ is an important inorganic material that has a high application potential in various fields, such as in photoluminescence, scintillator materials, magnetic properties, and microwave applications. Its optical properties have been studied intensively [10–13]. Its unique combination of physical and chemical properties, in terms of molecular and electronic versatility, reactivity, and stability, make us have reason to believe it may be a promising photocatalyst. However, the investigation on the photocatalytic activity of $ZnWO_4$ has never been reported before. It is, therefore, of great interest to examine the photocatalytic properties of pure $ZnWO_4$ material.

Most previous approaches to the preparation of $ZnWO_4$ material need high-temperature and harsh reaction conditions, such as the solid-state metathesis reaction [14] and sol–gel method [15]. Recently, environmentally friendly aqueous processes have received much attention [16–19]. This includes the processes in which materials are synthesized under mild conditions in nonharmful solvents such as water. The successful sample of $ZnWO_4$ microcrystals prepared by the hydrothermal method has also been reported [20–22]. Obviously, the suitable synthetic approaches may give rise to differing photochemical properties due to possible variation of surface morphology and structure. To our knowledge, this approach offers many advantages over conventional solid-state methods, such as mild synthesis conditions, high degree of crystallinity, high purity, and narrow particle size distribution of product. More importantly, much higher efficiency of the photocatalyst synthesized by this method could be expected from the special nanostructure of the material. In our previous reports, Bi_2WO_6 nanosheets showed the enhanced photoactivity for the decomposition of the pollutant [17,18].

The present work has been directed toward the synthesis of $ZnWO_4$ catalyst. Both the aqueous RhB and the gaseous FAD photodegradation were employed as the probe reaction to test the photoactivity of the as-prepared samples under UV

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* Corresponding author. Tel.: +86 10 6278 3586; fax: +86 10 6278 7601.
E-mail address: zhuyf@mail.tsinghua.edu.cn (Y. Zhu).

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irradiation. For the most active sample synthesized at 180 °C for 24 h, the generation of photocurrent and H_2 evolution from water was also observed. As far as we know, this is the first fruitful attempt to observe the photoactivity of $ZnWO_4$ catalyst.

2. Experimental

2.1. Catalysts preparation

$ZnWO_4$ was prepared by hydrothermal synthesis. The details are as follows: 0.001 mol $Na_2WO_4{\cdot}2H_2O$ and 0.001 mol $Zn(NO_3)_2$ were added to 9 mL deionized water with magnetic stirring to form a homogeneous solution. The solution pH was adjusted to 11 by using 0.5 M NaOH or HCl. The reaction mixture was then sealed in a 50 mL capacity Teflon-lined stainless steel autoclave, and was heated under autogenous pressure at a series of temperatures for 24 h or at 180 °C for a series of aging time in a digital-type temperature-controlled oven. After cooling, the product was filtered, washed, and dried at ambient temperature.

Particulate TiO_2 (P-25 and anatase) was commercially available from American Instrument Co. (AIC). Degussa P-25 TiO_2 was a mixture of 75% anatase and 25% rutile. Its BET surface area was about 50 $m^2\,g^{-1}$. The anantase TiO_2 was a pure phase free of rutile according to XRD pattern, and it has a BET surface area of 10.3 $m^2\,g^{-1}$. All chemicals were reagent grade quality and were used without further purification. All aqueous solutions were made up in deionized and doubly distilled water.

2.2. Sample characterization

Morphologies and microstructures of the as-prepared samples have been determined using a JEOL JEM 1010 transmission electron microscope (TEM) operated at an accelerating voltage of 120 kV. The samples were prepared by dispersing the powders in water and depositing a drop of suspension onto a thin Formavar film supported on a Cu grid. X-ray diffraction (XRD) patterns of the powders were recorded at room temperature with a Bruker D8-advance X-ray diffractometer at 40 kV and 40 mA for monochromatizaed CuKα radiation. Diffraction patterns from powdered samples held on quartz zero-background plates were obtained by θ–θ geometry. Visible-ultraviolet spectra were obtained using a Hitachi U-3010 spectrometer. $BaSO_4$ was the reference sample and the spectra were recorded in the range 200–700 nm. Total organic carbon (TOC) was measured with a Tekmar Dohrmann Apollo 9000 TOC analyzer. NH_4^+ and NO_3^- ions were analyzed with an ion chromatograph (Shimadzu LC-10AS).

2.3. Photochemical experiments

The photocatalytic activities were firstly evaluated by the decomposition of rhodamine-B (RhB) during irradiation with UV ($\lambda = 254$ nm). UV light was obtained by a 12 W Hg lamp (Institute of Electric Light Source, Beijing) and the average light intensity was 150 $\mu W\,cm^{-2}$. The irradiation area was approximately 40 cm^2. The radiant flux was measured with a power meter from the Institute of Electric Light Sources (Beijing, China). Aqueous suspensions of RhB (usually 100 mL, 1×10^{-5} M) and 50 mg of the powder were placed in a vessel. Prior to irradiation, the suspensions were magnetically stirred in the dark for ca. 30 min to ensure the equilibrium of the working solution. The suspensions were kept under constant air-equilibrated conditions before and during the irradiation. pH of the reaction suspension was not adjusted. At given time intervals, 3 mL aliquots were sampled, and centrifugated to remove the particles. The filtrates were analyzed by recording the variations of the absorption band maximum (553 nm) in UV–vis spectra of the dyes using a Hitachi U-3010 spectrometer.

To further evaluate the photocatalytic activities of this material, we tested oxidative decomposition of gaseous formaldehyde (FAD) under UV irradiation ($\lambda = 254$ nm). A 50-mg sample was evenly and uniformly spread without open spaces in the sample over the irradiation area (approximately 9.4 cm^2) in a 250 mL vessel. So, in this experimental condition, irradiated light was absorbed only on the outer geometric surface of the powder. A controlled concentration of the reactant gas was injected into the vessel and then the samples were stored in the dark condition. After the confirmation that the FAD gas concentration was kept constant, the light irradiation started. The amounts of FAD were determined using a gas chromatograph (SP-502) with FID.

For photoelectrochemical measurements, a Cu wire was attached to $ZnWO_4$ thin film with ITO substrate with epoxy resin to prevent current leakage. A Pyrex electrolytic cell was employed, filled with 100 mL of N_2-purged 0.5 M Na_2SO_4 solution. A Pt wire and a saturated calomel electrode (SCE) were employed as the counter and reference electrodes, respectively. Each $ZnWO_4$ thin film with ITO substrate was placed 3 cm in front of a 20 W germicidal lamp (~90% of energy output at 254 nm). The intensity of light was 1 $mW\,cm^{-2}$ at 4 cm into the reactor, the position where the film electrode was placed. The photoelectrochemical experiment was carried out with a computerized CHI660B electrochemical system (Shanghai, China).

Photocatalytic H_2 evolution from pure water (400 mL) dispersed with RuO_2 (1.0 wt%)/$ZnWO_4$ (0.3 g) under UV light irradiation was carried out in an inner irradiation quartz cell. The production of H_2 from aqueous CH_3OH solution dispersed with Pt (1.0 wt%)/$ZnWO_4$ (0.544 g) was also observed. The sacrificial reagent methanol (50 mL) was taken as an electron donor. The light source was a 400 W high-pressure mercury lamp (RIKO 400HA). With an increase of irradiation time, gases were evolved, and the gas pressure was increased. The gases were in situ analyzed with a TCD gas chromatograph (Shimadzu GC-8AIT, argon carrier), which was connected to the closed gas circulating line.

2.4. DFT electronic structure calculations

The quantum-mechanical calculations performed here are based on density functional theory (DFT) [20]. Exchange-